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# TEXTBOOK OF HEAT

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LONDON

UNIVERSITY TUTORIAL PRESS LTD

CLIFTON HOUSE, EUSTON ROAD, N.W. 1

## PREFACE

THE object of this book is to provide a comprehensive course on the theory of Heat mainly of Intermediate University standard: the requirements of such a course have not been rigidly adhered to however in cases where the importance of the subject and its modern development seemed to necessitate some extension. The work is based largely on previous editions of the well-known book published under the authorship of Professor J. Satterly and the late Dr. R. Wallace Stewart by the University Tutorial Press.

The book has been carefully revised and largely rewritten, most of the diagrams in the text have been redrawn and a number of new ones incorporated, the type has been completely reset, and the whole format of the book has been modernised and rendered more attractive to the reader. Whilst retaining much of the subject-matter and the mode of treatment contained in the previous editions, the work has, to a certain extent, been rearranged in an order which the wide teaching experience of the present author has shown to be the most logical, and many additions have been made.

Amongst the additions, the most important are sections on Gas Thermometry, Specific Heat of Liquids and Gases, Mechanical Equivalent, Thermodynamics, Thermal Conduction, including descriptions of modern laboratory methods of determination where necessary, and a chapter on the Kinetic Theory of Gases. Exercises and examination questions, as well as the Tables of Physical Constants, have been revised and grouped together at the end of the book, instead of being contained in the text.

The examination questions have been selected from examination papers set during the past five years by the University of London

## PREFACE

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for the Intermediate examinations in Science and in Engineering. The author gratefully acknowledges the permission to reproduce such questions granted by the Senate of the University.

The author also expresses his sincere thanks to Mr. R. W. Hutchinson, M.Sc., for his ever-ready help and useful criticism during the preparation of the book, and to friends and colleagues who have made useful suggestions.

C. T. A.



*This book is produced in  
complete conformity with the  
authorised economy standards.*

*Second Edition 1939*

*Reprinted 1942*

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# TEXTBOOK OF HEAT

## CHAPTER I

### INTRODUCTORY

**I**N everyday life *hot* and *cold* bodies are distinguished by the sense of touch; and, in the same way, it is a familiar fact that one body may be *hotter* or *colder* than another, or that the same body may become *hotter* or *colder*.

#### 1. Sense of Heat

When a substance hotter than the hand is touched, the sensation of heat is experienced, and it is said that heat passes from the substance to the hand. In the same way, when a substance colder than the hand is touched, the sensation of cold is experienced, and it is said that heat passes from the hand to the substance. In either case, the intensity of the sensation depends upon the extent to which transfer of heat between the hand and the substance takes place, and, as will be seen later, this depends not only upon how hot or cold the substance is, but also upon the nature of the substance.

Sensation, however, is not always a safe guide in determining the relative hotness or coldness of bodies. Thus, if the right hand be placed in hot water and the left in cold water for a short time and then both are plunged simultaneously into lukewarm water, this will feel hot to the left hand and cold to the right hand. This shows that in interpreting sensations of heat and cold the previous state of the hand, or other organ of touch, must be considered.

Again, in the hot room of a Turkish bath all the objects are equally hot and hotter than the body. To the sense of touch, however, all objects made of good conducting material, such as metal, appear to be much hotter than objects made of poor conducting material, such as wood. This, as explained later, is due to the fact that in the case of good conducting materials the transfer of heat to the hand is greater and more rapid than in the case of poor conducting materials. Similarly, on a cold day an object of iron out of doors will appear much colder than an object of wood, owing

to the fact that heat is transferred more readily from the hand to the iron, which is a good conductor, than to the wood, which is a poor conductor.

These illustrations show that in interpreting sensations of heat and cold, the nature of the substance touched must be considered as well as the state of the organ of touch.

The sensations referred to above are those due to actual contact with a hot or cold body. The sensations of heat experienced in the *neighbourhood* of hot and cold bodies are usually due to radiation (see Chapter XVII.).

## 2. Temperature

Instead of saying that a body becomes hotter or colder it may be said that a body acquires higher or lower degrees of hotness. Degrees of hotness below a certain standard, commonly that of the human body, might perhaps be spoken of as degrees of coldness, but it is more convenient to use one term—hotness—as applicable throughout the whole range. To speak of degrees of hotness is, however, clumsy and inconvenient. The term **temperature** is therefore used to deal with the idea of degree in relation to hotness. When a body has acquired any particular degree of hotness it is said to be at a particular temperature, and as a body becomes hotter its temperature is said to rise, and as it cools its temperature is said to fall. The word **temperature** thus means simply the degree of hotness of a body measured according to some arbitrarily chosen scale.

## 3. Difference of Temperature

It is a matter of common experience that when a hot body is placed in contact with a colder one, the hotter body becomes colder and the colder body becomes hotter. In such a case it is said that "heat" has passed from the hot body to the cold one. Thus, if a cold piece of metal is placed in contact with a hot piece heat passes from the hot piece (which is at the *higher temperature*) to the cold piece (which is at the *lower temperature*) until the two pieces attain the same temperature. The **difference of temperature** between two bodies A and B is therefore defined as that condition which is essential for the transfer of heat to take place from A to B or from B to A. If two bodies are at different temperatures, then when they are placed in contact heat passes from the body at higher temperature to the body at lower temperature. Or, if two

portions of the same body are at different temperatures, heat passes from the portion at higher temperature to the portion at lower temperature. Further, if two bodies are at the same temperature no heat passes from one to the other when they are placed in contact.

The transfer or exchange of heat between bodies not in contact belongs to the subject of radiation. (See Chapter XVII.)

#### 4. Nature of Heat

When a substance is heated it is said to gain or absorb *heat*. When it cools it is said to lose or give out *heat*. The question at once arises as to what is the nature of what is here called heat. It is evidently not material, for the mass of a body does not change as it gains or loses heat. The question is dealt with in Chapter XII., but it may be stated here, briefly, that whenever heat is produced energy in some form or other disappears, and, in accordance with the theory of transformation of energy, it is recognised that this energy has been transformed into heat—and that **heat is therefore a form of energy**. Thus when coal burns in air the chemical energy of the products of combustion is less than that of the original coal and air concerned, and the quantity of chemical energy so “lost” merely appears as the energy of heat. Similarly, when a piece of metal is hammered the energy used by the wielder of the hammer is not lost, but is found as heat in the piece of metal and in the hammer.

Hence, *as a body is heated it gains energy in the form of heat, and as it cools it loses energy in the form of heat.*

According to modern theory, the molecules of any given body are vibrating to and fro, at a rate dependent on the temperature, and the sum total of the kinetic energy of its molecules, due to this vibratory motion, determines the *molecular kinetic energy* for any temperature. As the temperature increases this molecular kinetic energy increases, as does also the potential energy of the system of molecules, and the total change in molecular energy accompanying any thermal change is equivalent to the heat generated or absorbed during that change.

The process of combustion is capable of a similar explanation. All chemical changes are due to molecular or atomic interaction, and it will be seen that the heat effect attending any chemical change may be due to a change in molecular energy resulting from this interaction.



### 5. Heat a Measurable Quantity

A quantity is that which can be expressed in terms of a fixed unit of its own kind, and its measure is the ratio of the given quantity to the chosen unit. Let us now consider if heat is, in this sense, a measurable quantity.

Suppose that a gas flame, whose rate of burning is absolutely uniform, is used. It may be assumed that its heating effect is equal for equal intervals of time. If now a fixed quantity of water, at a given temperature, is heated by this flame for a given time, its temperature will be raised to a certain degree, indicating the absorption of a definite quantity of heat. An exactly equal quantity of water will, in the same circumstances, reach the same temperature in the same time, and will therefore absorb the same quantity of heat. Hence, if double the quantity of water is heated under precisely similar conditions, it will be raised to the same temperature in double the time—that is, after the absorption of double the quantity of heat. If, therefore, the quantity of heat absorbed in either of the cases first considered is taken as the *unit*, the measure of the quantity of heat absorbed in this last case is 2.

Heat may thus be considered as a measurable quantity. The unit adopted in its measurement is quite arbitrary. For example, the unit might be taken to be the quantity of heat required to raise one pound of water from one particular temperature to another. Then, the measure of the quantity required to raise  $m$  pounds through the *same* range of temperature would be  $m$ . This subject will be considered further in Calorimetry. (See Chapter VII.)

### 6. General Effects of Heat

When a body is heated or cooled sufficiently, various well marked effects are generally produced. The more important are included under the following heads: (1) Change of temperature, (2) Change of volume—expansion or contraction, (3) Change of state, (4) Change of physical properties, (5) Promotion of chemical action.

(1) CHANGE OF TEMPERATURE.—This is almost axiomatic, for it has been assumed that if the temperature of a body is rising, it is absorbing heat. It is true, however, only when a body is not changing its state.

When water is boiling, its temperature remains constant; extra heat given to the water is used in changing some of the water to

steam, and the temperature of the steam is still the same as that of the water. Again, when water is being frozen, heat is removed from the water, but the mixture of ice and water still remains at the freezing point, and not until all the water has been frozen is it possible for the ice to get colder than this temperature. When, however, a substance remains in one definite state—solid, liquid, or gaseous—gain of heat produces an increase of temperature, loss of heat produces a decrease of temperature. Conversely, a rise in temperature indicates a gain of heat, and a fall in temperature a loss of heat.

(2) CHANGE OF VOLUME.—It is found that in general when a body is heated it expands, and will, if allowed to cool to its original temperature, gradually contract to its original volume. This is the same whether a body is a solid, a liquid, or a gas. Exceptions to the general rule are silver iodide, Rose's fusible alloy and some other alloys, and water below  $4^{\circ}\text{C}$ . The amount of expansion is different for different bodies: in general, gases expand more than liquids, and liquids more than solids, for the same rise of temperature. A few simple experiments will illustrate this expansion by heat.

*Experiments.* (a) The historical Gravesande's Ring and Ball is shown in Fig. 1. The ball when cold will pass through the ring. When heated it will not pass through the ring. If allowed to rest in position and cool, its dimensions in time become smaller than the ring and it falls through.

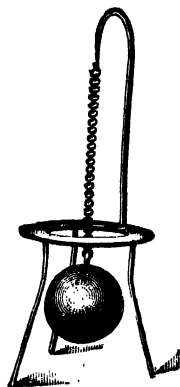


FIG. 1.

(b) In Fig. 2 I is a flat strip of brass about 18 in. long, one end being screwed to the wooden block B, and the other end resting on a needle VV on the top of the wooden block A. A pointer PP of straw is attached by sealing-wax to the needle, and behind the pointer is a graduated circular scale. W is a weight for steadying purposes. On heating the rod the pointer moves over the scale and finally takes up a position of rest. This movement is due to the needle rotating, and the cause of the rotation is the expansion of the rod. If the rod be allowed to cool it contracts, and the pointer moves back to its former position.

In the case of liquids, which must be in an envelope, the expansion is complicated by that of the vessel. The following shows the change of volume of a liquid.

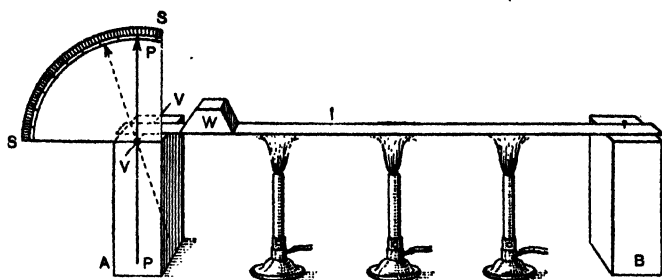


FIG. 2.

(c) A small flask (Fig. 3) is fitted with a stopper through which passes a piece of coarse *capillary* tubing. The flask is first filled with alcohol coloured by a little magenta dye and then the stopper is inserted so that the liquid rises a short distance in the tube. The flask is placed in a beaker of hot water. The liquid expands and rises in the tube.

(d) In Fig. 4 the flask is fitted with a stopper through which a piece of glass *quill* tubing passes nearly to the bottom. A little coloured alcohol is placed in the flask so that the end of the tubing dips into it. If the flask be held in the hands the heat imparted causes the *air* in the flask to expand, forcing some of the alcohol up the tube.

(3) CHANGE OF STATE.—Bodies may exist in three states—solid, liquid, and gas—and the change from one to the other may always be effected by the application or withdrawal of heat. Thus, for example, if ice is heated it melts into water, and if water is heated sufficiently it boils and becomes steam. The reverse of the process is the withdrawal of heat from steam, when it condenses to water, and the withdrawal of heat from water, when ice is formed. Again, air is a gas under usual conditions, but if subjected to intense cold it can be liquefied and even solidified.

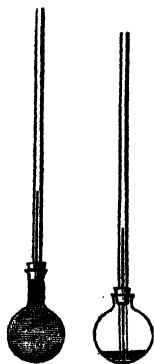


FIG. 3. FIG. 4.

(4) CHANGE OF PHYSICAL PROPERTIES.—It is found that heating and cooling modify in many ways the properties of matter. Iron heated to redness differs materially from iron at ordinary

temperatures; steel may be softened or tempered by heating and cooling. Again, some bodies change colour on being heated: thus, mercuric iodide is red at ordinary temperatures, but changes to yellow when heated. The elasticity and rigidity of solids, the viscosity of liquids, the ease with which a substance conducts electricity, and, in fact, all the characteristic physical properties of matter change with change of temperature.

(5) CHEMICAL CHANGE.—It is well known that heat frequently tends to promote chemical action. Thus coal, wood, sulphur, magnesium, and many other substances when heated with free access of air combine vigorously with the oxygen of the air—the phenomenon of *combustion* or burning, which is simply oxidation, accompanied by a large output of heat. Also coal, wood, and other substances, when heated alone in a closed space, undergo decomposition and give rise to various products; thus, coal gives rise to coal-gas and coal-tar.

## CHAPTER II

### THERMOMETRY

WHEN it has been said hitherto that an object was *hot*, it was meant that when touched with the hand heat flowed from it to the hand; and when another object was said to be *cold*, it was meant that when touched heat flowed from the hand to it. The *criterion* therefore, was the temperature of the hand, and the interpretations were based on *sensations*. But to this method of estimating temperature there are, as already will have been surmised, three serious objections: (1) the sensations are not sufficiently delicate, (2) they do not admit of numerical measurement, (3) the criterion (the temperature of the hand) is variable.

It is necessary, therefore, to have more certain means of comparing temperatures, and instruments called **thermometers** have been devised for this purpose. *A thermometer is an instrument for the comparison and measurement of temperature.*

#### 1. Preliminary Idea of a Thermometer

It has been noted that the effects of heat on matter are very diverse. The one which lends itself most readily to the measurement of degree of hotness, or temperature, is that of change of volume, or expansion. So long as no change of state occurs, expansion, in most substances, is simultaneous with change of temperature, and change of length or change of volume may be taken therefore to indicate change of temperature. Also, a particular length of any given rod or a particular volume of any given quantity of liquid corresponds to a particular temperature and may be taken as an indication of that temperature.

Thus with a flask and tube as used in Exp. (c), page 6, the changes in the volume of the liquid are clearly indicated, and with a large bulb and a tube of very narrow bore an instrument capable of indicating very small changes of volume and therefore of temperature may be constructed. In practice, a glass flask or bulb filled with mercury is found to work most satisfactorily and is used invariably if the temperature to be measured is likely to rise nearly as high as that of boiling water.

If the indicator be provided with a scale etched on the tube its readings can be noted and compared more readily, and the usefulness of the instrument is increased greatly. The scale adopted may be quite arbitrary. A scale of millimetres would serve, for example, but evidently it would be an advantage if the scale were arranged to indicate degrees of temperature in accordance with some generally understood and easily realised scale.

Such a scale may be obtained as follows: Let the temperature indicator be placed in melting ice, and when the position of the liquid column in the tube is steady, let it be marked by a fine scratch on the tube. This mark indicates the temperature of melting ice, which by experiment is found to be a constant, naturally fixed temperature. Then, let the indicator be placed in steam from water boiling under the normal atmospheric pressure, and when the liquid column is again steady let its position be marked. This second mark indicates the temperature at which water boils under the normal atmospheric pressure, and this again by experiment is found to be a constant, naturally fixed temperature. These two temperatures are known generally as the **freezing point** and **boiling point** of water, and from these two *fixed points* a scale is derived readily.

## 2. The Principle of Graduation of a Scale of Temperature

The range of temperature between the *freezing point* and the *boiling point* may be divided into any number of steps by dividing the volume of the tube into a corresponding number of equal parts. For example, the range of temperature from freezing point to boiling point may be divided into 100 steps or *degrees* by dividing the volume of the bore of the tube between the two marks corresponding to these temperatures into 100 equal parts.

It should be noted carefully here that *nothing is said about dividing the range of temperature into 100 equal parts*. The volume of the tube bore between the two marks is divided into 100 equal parts, but the corresponding steps or degrees of temperature indicated by these divisions may or may not be equal, and are determined by and vary with the expansibility of the liquid used in the indicator. For example, if two indicators are made accurately and graduated in the way here described they will give usually two different scales of temperature; that is, if both were placed together in a bath where the temperature is raised gradually from freezing point to boiling point, it is probable that the temperature readings would agree exactly only at the fixed points. The

question that arises here is not which is correct, but which is to be adopted as the standard; that is, which is to be set up as correct by definition and common convention. Hence, if an indicator of this type is to be used as a standard instrument for general reference the liquid and the material of the bulb and tube must be specified. An instrument constructed and graduated on this principle, to indicate temperature with reference to an arbitrary selected scale, is known as a *thermometer*.

Certain substances are suited better than others for the measurement of temperature. A body which changes volume only to a small extent for a large variation of temperature is not suitable. Solids are not used because their changes in volume even when heated or cooled considerably are minute. Gases change volume very readily when exposed to different temperatures, and for certain purposes a gas thermometer is a useful instrument. Liquids are, however, the best adapted for ordinary thermometry.

Of liquids, *mercury* is the best for all general purposes, because it boils at a very high, and freezes at a very low, temperature. Hence, it remains liquid through a long range of temperature. Mercury has other advantages: it quickly assumes the temperature of anything in which it is immersed without abstracting much heat from the substance, and it does not soil glass. *Water* has a comparatively small range of temperature between its freezing and boiling points. *Alcohol* is useful for very low temperatures at which mercury would be frozen, and it is used also in some self-registering minimum thermometers, but it cannot be used for high temperatures because it boils at a temperature lower than the boiling point of water. Standard thermometers are usually mercury-in-glass thermometers with a scale engraved on the glass stem.

### 3. Construction of a Mercury-in-Glass Thermometer

The usual laboratory method of constructing an ordinary mercury thermometer is given here.

(1) PREPARING THE TUBE.—A length of thick-walled capillary tubing, having as uniform a bore as can be found, is taken and well washed, first with a solution of potassium bichromate in sulphuric acid and then with distilled water, and finally dried by a current of hot air. Before proceeding to construct the instrument, it is well to make a preliminary test of the uniformity of the bore of the tube chosen. For this purpose, a short thread of mercury about an inch long is introduced by suction into the tube. With a

little skill, a thread of the desired length may be got into the bore and moved into any part of the tube. This done, the length of the thread is measured by suitable means in a particular position in the tube; the thread is then moved into some other position and again measured, and so on. If the length remains constant for different positions, it is evident that the bore must be perfectly uniform. If, however, the differences in length are very great the tube must be rejected and another tried. When a suitable tube is obtained, one end is heated till melted and is then blown into a bulb. The size of the bulb is determined by the purpose the thermometer is intended to serve. The larger the bulb the longer will be the degrees on the scale of the completed thermometer.

(2) INTRODUCING THE MERCURY.—In order to introduce mercury into the bulb, a funnel-shaped reservoir is made at the other end of the tube (Fig. 5), or a small funnel is attached to the tube by means of an india-rubber joint. Such thermometer tubes can be bought ready-made. More than sufficient mercury to fill the bulb is poured into the reservoir, and the bulb is heated gently so that the air in it expands, some of it escaping by bubbling through the mercury. It is then allowed to cool, and as the air contracts a small quantity of the mercury from the reservoir enters the bulb. This process of alternate heating and cooling is continued until the bulb is about half full of mercury. Then the bulb is heated gently until the mercury boils and its vapour expels the air, which bubbles through the mercury in the reservoir. All traces of air and moisture are thus removed, and when cool the mercury forms a continuous column filling the bulb, tube, and part of the reservoir.

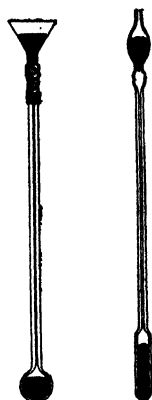


FIG. 5.

While still warm the excess of mercury in the reservoir is poured off, the tube is heated at a point just below the reservoir and drawn out so as to greatly constrict the bore. Then the bulb is heated a little above the highest temperature the thermometer is intended to indicate. The mercury now fills completely the tube or stem, and while it does so a blow-pipe flame is directed on the constriction, the upper part of the tube is drawn off, and the thermometer finally closed.

The instrument is now ready for graduation, but it is better to keep it two or three weeks before proceeding with this, because



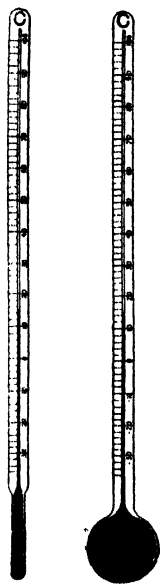


FIG. 6.

when glass has been heated to a high temperature, it takes a long time to recover its original volume. If greater accuracy is desired, the thermometer should be kept for several months before graduation. The usual forms of a mercury-in-glass thermometer are shown (Fig. 6).

(3) DETERMINING THE FIXED POINTS.—As a preliminary to graduation it will be necessary to mark on the stem the position of the mercury thread corresponding to the two standard temperatures referred to above as the freezing point and boiling point of water. The lower fixed point is referred to as the *freezing* point, though in reality it is the *melting* point of ice, not the freezing point of water. The freezing point of water is, in fact, not constant, but is influenced by several circumstances.

*The freezing point.* To determine this point the thermometer is placed in a vessel, and the bulb and the lower part of the stem are surrounded completely by melting ice (Fig. 7). A funnel may be used for this purpose, but this is unnecessary, for so long as any ice remains in the vessel the temperature is that of the freezing point. When the level of the mercury becomes perfectly stationary a fine mark is made on the stem at the extremity of the column. This is one of the fixed reference points on the scale and indicates the temperature of melting ice.

*The boiling point.* In order to mark this second point on the thermometer a hypsometer (Fig. 8) is used. It is made of copper, and the steam from water boiling in the lower part circulates round the double casing of the upper part, and finally escapes by a side tube near the bottom of the outer casing. The thermometer is passed through a cork and placed in the apparatus in the position indicated. After some time the mercury becomes stationary, and the thermometer is adjusted so that the top of

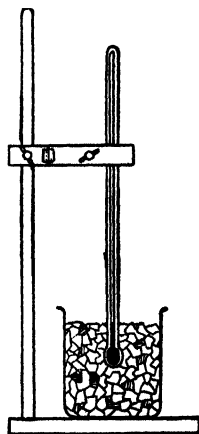


FIG. 7.

the mercury column is seen just above the cork; its position is then marked and the second reference point on the scale is thus determined. It indicates the temperature of steam from water boiling under the atmospheric pressure given by the barometer at the time of the determination. For the present it will be supposed that this pressure is normal. (Note that a hypsometer is not necessary, except for the most accurate work: a flask with a long neck may be used.)

It should be noted that the thermometer is placed in the steam and not in the boiling water. The temperature of boiling water depends on various circumstances, whereas the temperature of the steam depends only on the pressure at which boiling takes place.

(4) GRADUATING THE THERMOMETER.—It remains now to graduate the space between the fixed points, and to continue the division throughout the whole length of the stem. A zero point is chosen, the divisions below it are marked negative, and those above positive.

There are three scales of graduation now in use; and as temperatures may be expressed in any one of these scales, it will be necessary to consider them. They are called the *Centigrade*, *Fahrenheit*, and *Réaumur* scales (Fig. 9).

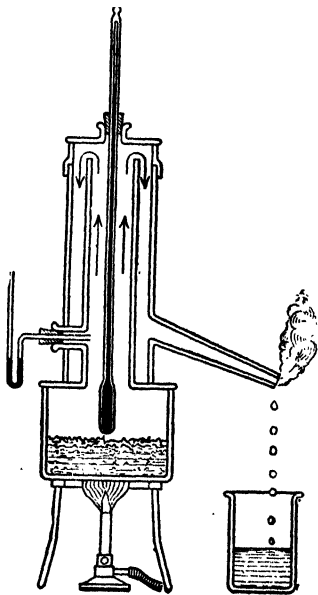


FIG. 8.

The *Centigrade* scale was introduced by Celsius, a Swede. On it the freezing point is taken as zero and marked  $0^{\circ}$ ; the boiling point is marked  $100^{\circ}$ . The space between the fixed points is thus divided into 100 equal divisions, called degrees. Graduation on the same scale is extended beyond the reference points; the divisions below zero—that is, below freezing point—are considered negative, and those above positive. This scale is the one most generally used for scientific purposes.

The *Fahrenheit* scale was introduced by Fahrenheit, of Danzig. On it the freezing point is marked  $32^{\circ}$  and the boiling point  $212^{\circ}$ .

the space between being divided into 180 equal degrees, and the division extended above and below the fixed points. Thus the zero is at a point  $32^{\circ}$  below the freezing point; it is supposed to be the lowest temperature obtained by mixing snow and salt. On Fahrenheit's original scale the upper fixed point was the temperature of a human being in normal health. In the early thermometers

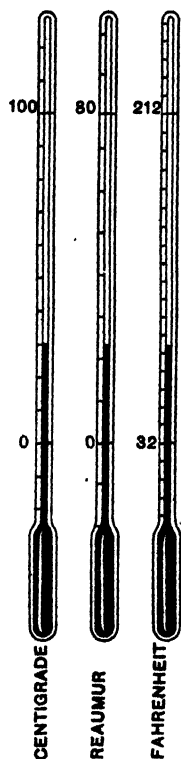


FIG. 9.

the interval between these two fixed points was divided into 24 equal parts, and later into 96. It was found subsequently that the 32nd degree corresponded to the melting point of ice, and the 212th to the boiling point of water. On the amended scale the temperature of a human being is  $98^{\circ}$ . This scale is very generally used in Great Britain for the purposes of ordinary life, and to some extent for those of science, especially in Meteorology.

On the third scale, invented by Réaumur, a Frenchman, the freezing point is taken as zero and marked  $0^{\circ}$ , and the boiling point  $80^{\circ}$ . There are thus 80 equal divisions between the fixed points on this scale. It is used in Germany for medical and domestic purposes, but is never used in England.

Having decided on the scale, the thermometer stem is coated with paraffin-wax and the scale scratched thereon. The stem is then exposed to the action of hydrofluoric acid, when the exposed part of the glass is etched. The wax is then removed by melting.

*A degree of temperature on any thermometric scale is the change of temperature corresponding to the expansion of the mercury in the thermometer from one division of the scale to the next. A particular temperature on any thermometric scale*

is the temperature indicated by a thermometer when the mercury in the stem stands at a particular division on that scale. For example, the temperature  $15^{\circ}$  C. is the temperature indicated when the mercury in the tube of a mercury-in-glass thermometer stands at the 15th division above zero on the Centigrade scale.

Note that, say  $-10^{\circ}$  C. is 10 degrees C. below the freezing point;  $-10^{\circ}$  F. is 42 degrees F. below the freezing point.

#### 4. The Fundamental Interval. Conversion of Scale Readings

The interval between the fixed points on a thermometer is called its *fundamental interval*. On the Centigrade scale this is equal to 100 divisions, on the Fahrenheit 180, and on the Réaumur 80.

It is sometimes necessary to convert temperatures expressed on one scale into the corresponding temperatures on one of the other scales. To effect this, it is necessary to remember that the range of temperature from freezing point to boiling point is the same on each scale, and that the freezing point on the Fahrenheit scale is 32 degrees above the zero of that scale, so that a temperature  $F$  on the Fahrenheit scale is  $(F - 32)$  degrees above the freezing point. It is also necessary to remember the magnitude of the fundamental interval of each thermometer scale, as well as the fixed points.

If, therefore,  $F$ ,  $C$ , and  $R$  denote corresponding temperatures on the Fahrenheit, Centigrade, and Réaumur scales, the following relation holds:—

$$(F - 32) : C : R :: 180 : 100 : 80$$

or

$$\frac{F - 32}{9} = \frac{C}{5} = \frac{R}{4}.$$

**Example.**—If a Fahrenheit and a Centigrade thermometer are placed in the same liquid, and the Fahrenheit instrument reads 68°, what is the reading of the Centigrade instrument?

The liquid is  $(68 - 32) = 36^\circ \text{F.}$  above the freezing point.

Thus, since  $(F - 32) : C :: 180 : 100$ ,

$$\text{or } \frac{F - 32}{9} = \frac{C}{5},$$

$$\text{Hence } \frac{36}{9} = \frac{C}{5},$$

$$\text{or } C = 20.$$

Therefore the reading of the Centigrade instrument is 20°.

In working such problems as this it is helpful to sketch two thermometers side by side (Fig. 10) in order to show that the scale of each thermometer is obtained by dividing proportionately the stem between the freezing and boiling points.

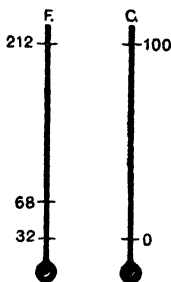


FIG. 10.

#### 5. Comparison of Mercurial Thermometers

From what has been said, it is clear that one important point aimed at in the construction of thermometers is that the indications given by different but similarly constructed instruments may be

comparable with one another, so that a temperature referred to by one experimenter may be reproduced by others wishing to do so. If it were possible to make all mercurial thermometers of the same glass, their indications would be strictly comparable. This is impossible, however; and further, it must be remembered that the construction of a thermometer is a difficult operation, and that, therefore, errors in construction are almost inevitable.

For these reasons mercurial thermometers are not strictly comparable, in practice, and it is usual to compare all thermometers likely to be used in important experiments with a standard thermometer. Such a standard is kept at the National Physical Laboratory, and any thermometer sent there for comparison is returned with a table of corrections, the application of which will make its indications or *readings* strictly comparable with those of any other instrument similarly compared.

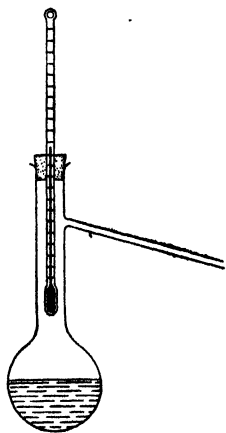


FIG. 11.

The freezing point of a thermometer may be tested by placing the instrument in melting ice as indicated on page 12. When the reading is constant the difference between the reading and the freezing point as marked is the *error* of the thermometer at this temperature. If the reading is above the freezing point the *correction* is negative, if below it is positive.

To test the boiling point of a thermometer a flask with a side tube (Fig. 11) or one fitted with a side tube (Fig. 12) may be used, and the method indicated on page 13 is followed. A few fragments of unglazed earthenware should be placed in the flask to prevent the water bumping as it boils. When the reading of the thermometer is constant it is recorded. To find the correction to be applied at this temperature, the boiling point of water under the existing atmospheric pressure must be obtained. By definition (see Chapter IX.) the temperature of steam from boiling water is  $100^{\circ}\text{C}$ . only when the barometer reads 760 mm. at  $0^{\circ}\text{C}$ . at sea-level in latitude  $45^{\circ}$ . The barometer must therefore be read. At sea-level in the latitude of London the temperature of boiling is approximately  $0.0367^{\circ}\text{C}$ . above or below  $100^{\circ}\text{C}$ . for each millimetre that the barometer (corrected to  $0^{\circ}\text{C}$ .) is above or below 759.6 mm. (Page 398.)

*Experiment.* To compare two graduated thermometers.—Place the thermometers A and B together in a large water-bath provided with a stirrer. One of the thermometers, A, is to be considered as the reference or standard instrument. Heat or cool the bath to definite temperatures as indicated by A, say  $0^{\circ}$ ,  $10^{\circ}$ ,  $20^{\circ}$ , etc. Record the corresponding readings of B. The changes of temperature must be effected very carefully and the bath stirred very well. In this way compare a Fahrenheit thermometer with a Centigrade. Plot (i) the readings of the Fahrenheit thermometer against those of the Centigrade; (ii) Fahrenheit temperatures equivalent to Centigrade. (The latter is a straight line:  $50^{\circ}\text{ F.} = 10^{\circ}\text{ C.}$ ,  $140^{\circ}\text{ F.} = 60^{\circ}\text{ C.}$ ) If the graph obtained in (i) is approximately a straight line, then the bore of B is almost as uniform as the standard. If the graph is definitely above or below the straight line of equivalent temperatures in (ii), it is likely that the scale has been badly made.

## 6. Other Simple Forms of Liquid-in-Glass Thermometer

For special purposes, various forms of thermometer are used. The more important of these are described below.

**THE ALCOHOL THERMOMETER.**—Alcohol is sometimes used instead of mercury in the construction of thermometers. It has the advantage that it can be employed for very low temperatures: mercury solidifies at  $-39^{\circ}\text{ C.}$ , whereas alcohol may be exposed to a very much lower temperature,  $-130^{\circ}\text{ C.}$ , without solidifying. It also expands much more, ten times more, than mercury for the same rise of temperature. The expansion of alcohol, however, is not uniform with temperature as indicated by a mercury-in-glass thermometer; the expansion increases with the temperature. For this reason, alcohol thermometers are usually graduated by direct comparison with a standard mercurial thermometer. Another advantage of alcohol is that an alcohol thermometer has a smaller capacity for heat than a mercury thermometer of equal sensitiveness.

A disadvantage of the alcohol thermometer is that if the top of the stem is colder than the bulb the alcohol has a tendency to distil

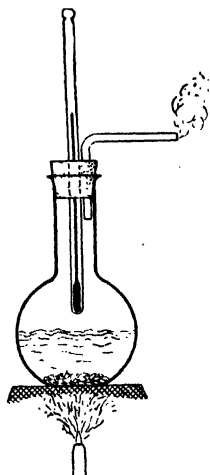


FIG. 12.

from the bulb into the top of the stem, thus rendering the graduations temporarily inaccurate. Also, as alcohol boils at  $78^{\circ}\text{C}$ ., temperatures higher than this cannot be determined.

Pentane is another liquid used in low temperature thermometers.

*Experiment. To graduate an alcohol thermometer.*—Immerse the thermometer successively in baths at  $70^{\circ}\text{C}$ .,  $60^{\circ}\text{C}$ ., down to  $0^{\circ}\text{C}$ . (ice and water), and  $-10^{\circ}\text{C}$ ., obtained by a mixture of ice and salt, as indicated by a standard thermometer. In each case mark the position of the alcohol surface with a piece of cotton tied tightly around the stem of the thermometer. Transfer the positions of the cotton rings to a card, and divide the spaces so that the scale may be read to degrees. Bind the card to the stem by fine wire.

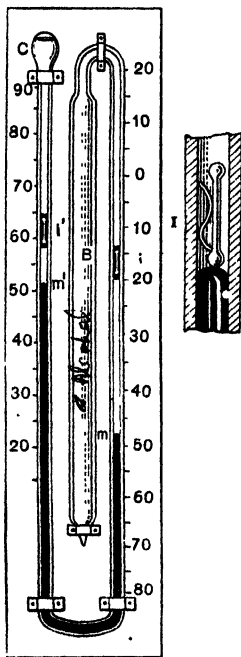


FIG. 13

**HIGH-TEMPERATURE THERMOMETERS.**—Mercury boils at  $357^{\circ}\text{C}$ . under normal pressure, and ordinary glass softens at high temperatures. In order to make thermometers which will read to high temperatures, up to  $550^{\circ}\text{C}$ . say, these difficulties are overcome by using a very hard glass (borosilicate) for the thermometer and filling the space above the mercury with nitrogen at a high pressure of 16 atmospheres to retard the boiling of the mercury.

In other forms of high-temperature thermometer, the mercury is replaced by the liquid alloy of sodium and potassium. This alloy, which looks very much like mercury at ordinary temperatures, is liquid between  $-8^{\circ}\text{C}$ . and about  $700^{\circ}\text{C}$ ., so that

between these limits it is particularly suitable for thermometry.

## 7. Maximum and Minimum Thermometers

It is often necessary to know the highest or lowest temperature reached in a given interval. For instance, it is usual in making meteorological observations to record the highest (maximum) temperature attained during the day and the lowest (minimum)

temperature reached during the night. For these purposes maximum and minimum thermometers are employed.

**SIX'S THERMOMETER.**—This is one of the oldest of its class and is at once a maximum and minimum thermometer (Fig. 13). The bulb B and part of the stem down to *m* is filled with alcohol. This is the real thermometric part of the instrument; the column of mercury, *mm'*, which occupies the U-tube merely acts as an index. Above *m'* the tube contains alcohol, as also does the lower half of the bulb, C. The upper half of C contains alcohol vapour only, thus leaving room for expansion. As the alcohol in B expands or contracts, the extremities, *m* and *m'*, of the mercury column rise or fall as the case may be, and the extreme point reached in each case is indicated by one end of a light steel index, *i* or *i'* (shown on a larger scale at I). This index is pushed before the mercury column and is prevented from returning by means of a spring, S, which is just strong enough to hold it in its place. The position of the index,

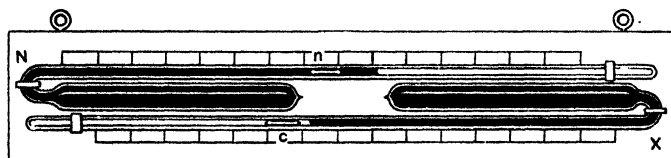


FIG. 14.

*i*, obviously indicates the minimum temperature reached, and that of *i'* the maximum temperature. When it is required to set the instrument ready for observations, these indices are brought into contact with the ends *m* and *m'* of the mercury column by means of a small magnet. This instrument is used largely by gardeners and nurserymen.

**RUTHERFORD'S THERMOMETERS.**—These are two separate instruments, but are usually mounted on the same frame (Fig. 14), in a horizontal position.

The maximum thermometer, X, is a modification of an ordinary mercurial thermometer. The maximum temperature is registered by means of a steel index, *c*, as in Six's instrument. As the thermometer lies horizontally there is no need to attach a spring to the index. The maximum temperature will thus be indicated by the position of that end of the index which is nearest the bulb of the thermometer.



The minimum thermometer, N, is an alcohol thermometer, and is the only minimum thermometer in general use. For registering the minimum temperature there is a small index, *n*, of glass or enamel, which allows the column of alcohol to expand past it without moving it; but when the alcohol contracts, the index, being wetted by the liquid, is drawn along by the surface film at the extremity of the alcohol column. The minimum temperature is thus indicated by the position of that end of the index which is furthest from the bulb of the thermometer.

The instruments are set by inclining the frame so as to cause the indices to slide down to the ends of the liquid columns. They are used largely by meteorologists.

**PHILLIPS' THERMOMETER.**—This thermometer (Fig. 15) is a mercury thermometer with a very fine bore, in which the column of mercury is broken by a small bubble of air which separates a short thread of mercury from the remainder of the column. This thread takes the place of the index in Rutherford's maximum thermometer. The instrument, which usually occupies a horizontal position, is set by placing it in a vertical position and gently tapping it. The bubble of air is thus reduced to its smallest dimensions, the gap in the column being about 1 mm. in length. When the mercury expands the index thread is pushed forward so long as expansion continues. When contraction takes place, the thread remains stationary, and the graduation is so arranged that the forward end indicates the maximum temperature experienced since the instrument was last set.

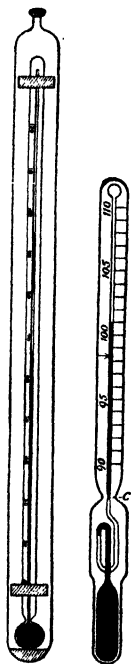


FIG. 15. FIG. 16.

**CLINICAL THERMOMETER.**—The ordinary clinical thermometer is a form of maximum thermometer. There is a constriction, *c*, in the stem (Fig. 16). When the mercury expands, it passes readily through the constriction, but when the mercury is cooling the column breaks at this point. The position of the upper end of the column left in the stem can thus be read at leisure. This thermometer is graduated to give a short range of temperature above and below the normal temperature of the body,  $98.4^{\circ}$  F. If placed in the mouth or arm-pit until it attains a steady temperature, its maximum reading gives the body temperature.

## 8. Very Sensitive Thermometers

When a salt is dissolved in water the temperature of the water is lowered. When the solution is heated to boiling, it is found that the temperature of boiling is higher than the temperature of boiling of pure water, and if the solution is frozen its freezing point is lower than that of pure water. In Physical Chemistry the measurements of the cooling produced by solution, the elevation of the boiling point, and the depression of the freezing point are of great importance, and sensitive thermometers have been devised for the purpose.

It is obvious that if a small difference of temperature is to be measured accurately, the bulb of the thermometer must be large in comparison with the volume of unit length of the bore of the stem. If the thermometer is to read actual temperatures over a wide range, this would necessitate a very long stem. However, it is not actual temperatures that are required, but only differences of temperature, so that a short-stem thermometer serves the purpose, provided that there is some means by which the end of the mercury column can always be brought within the limits of the scale.

An instrument specially designed for this work is *Beckmann's thermometer* (Fig. 17). It will be seen that the stem at the top of the tube is turned over and enlarged into a reservoir into which the excess mercury can be driven. Suppose, for example, that with the thermometer shown, the stem of which covers a range of  $6^{\circ}\text{C}$ . and which reads to  $0.01^{\circ}\text{C}$ ., it is required to measure the lowering of temperature when common salt is dissolved in water. The thermometer is heated to a temperature a little higher than the water so that the mercury column expands into the reservoir. The thermometer is now placed in the water, and the mercury column will come back to rest just below the upper limit of the scale. The salt is mixed with the water, the solution well stirred, and the cooling observed.

It will be noticed that the stem of such a thermometer is a tube of very small bore, and is protected by an enclosing tube fused to the bulb of the thermometer. The scale is engraved on a piece of milk glass which fits behind the stem, between it and the outer tube. The walls of the bulb are very thin so that the mercury quickly



FIG. 17.

reaches the temperature of the bath in which it is placed. Obviously the scale of such a thermometer must be calibrated by comparison with a standard thermometer. The quantity of mercury in thermometric use differs in different experiments, but the difference is so small that no correction to the size of the degrees is required on this account.

### 9. Sources of Error in a Mercurial Thermometer

The more important sources of error in connection with mercurial thermometers are as follows:—

(a) *Change of zero.* In many cases, if an ordinary thermometer which has been made for some time is placed in melting ice, it is found that its indication is a little higher than the freezing point marked on the scale. The reason for this is referred to in Art. 3 (2), page 12. If the thermometer tube has not been kept long enough before graduation, the gradual contraction of the bulb after graduation causes its interior volume to decrease, and consequently the volume of mercury contained at  $0^{\circ}\text{C}.$ , although constant, appears to increase, and the level of the column corresponding to the freezing point rises. To correct this error, it is necessary to re-determine the freezing point from time to time, and to deduce the observed error from any reading made. Thus, if zero is found to be at  $0.1^{\circ}\text{C}.$  some months after graduation, and the reading of the thermometer when placed in a bath of water is  $64.5^{\circ}\text{C}.$ , the correct temperature of the bath is  $64.4^{\circ}\text{C}.$

(b) *Recent heating.* This is a temporary source of error arising from the same cause as *change of zero*. If a thermometer is heated to a high temperature and then allowed to cool, the bulb will have for some time a larger volume than the normal. Hence, if the thermometer is placed in a liquid of lower temperature, the mercury will not rise to the same graduation as it would normally, and the temperature it indicates will be lower than the true temperature of the liquid. Therefore, the same thermometer must not be used for measuring low temperatures soon after it has been used for high temperatures. The error is merely temporary, and is quite inappreciable after a few days.

It is for this reason that, in the construction of thermometers, the freezing point is determined before the boiling point; if the latter were determined first, and the former soon after, the zero would be marked too low on the scale and would gradually rise, as explained in (a) above.

(c) *Boiling point.* The temperature of steam depends on the atmospheric pressure under which boiling takes place. At 760 mm. of mercury at  $0^{\circ}\text{C}$ ., at sea-level in latitude  $45^{\circ}$ , it corresponds to  $100^{\circ}\text{C}$ . or  $212^{\circ}\text{F}$ .; but if the pressure at the time of graduation is greater or less than this, the boiling point indicates a temperature higher or lower than this temperature.

Tables have been drawn up from experiments by Regnault, giving the boiling points of water corresponding to a wide range of pressures (see Table XV., page 398). Hence, if the barometric height is read at the time of determining the boiling point, the temperature corresponding to this pressure can be obtained from these tables, and the graduation carried out accordingly.

(d) *Temperature of the stem.* When a thermometer is used to determine a temperature, it is often impossible to subject more than the bulb and a small portion of the stem to this temperature. The upper portion of the stem is thus at a different temperature from the rest of the thermometer, and consequently the reading will be slightly different from what it would be if the whole thermometer attained the temperature it is intended to indicate. If the temperature of the bath is higher than that to which the stem is exposed the reading is too low, and if the temperature of the bath is lower than that of the stem the reading is too high. Approximate calculable corrections can be applied in both cases, and will be dealt with in the chapter on the Expansion of Liquids (Chapter V.). In some cases the correction may be considerable.

(e) *Position of thermometer.* A thermometer should be read always in the position in which it was graduated; for, if the bore of the stem is very small and the walls of the bulb thin, the influence of the pressure due to the contained mercury on the volume of the bulb may cause an appreciable change in the reading when the position of the instrument is altered. It is obvious that the reading will be lowest when the thermometer is held vertically.

(f) *Inequality of bore.* Ordinary thermometers are graduated by dividing the stem between the two fixed points into a number of equal parts. This method is satisfactory if the bore is exactly uniform, but is obviously incorrect if the bore is larger at some parts than at others. Two methods are available for arranging that the readings shall indicate temperatures correctly. The first method is to graduate the bore so that the volumes between the marks are equal. The second method is to graduate in equal

lengths, as stated above, and then test the uniformity of the bore in order to find the corrections which must be applied at each division to give the correct temperature. Particulars of these methods will be found in treatises on Practical Physics.

(g) *Minor errors.* Theoretically, corrections should be made for the pressure of the atmosphere at the time of determining the freezing point, and also for the influence of external pressure on the volume of the bulb; but these sources of error are quite inappreciable, under suitable conditions.

From what has been said above, it is obvious that it is not an easy matter to measure any particular temperature accurately, say to one-thousandth of a degree. It is, however, comparatively easy to measure accurately difference of temperature to this extent.

## 10. The Gas Thermometer

When it is considered what should be the properties of a perfect thermometric substance, it is found that air, or some similar gas such as nitrogen or hydrogen which closely conforms to Boyle's Law, comes nearest to the required standard, and is sometimes used when very accurate measurements are required.

The gas thermometer will be considered fully when dealing with the expansion of gases (Chapter VI.). It depends on either (a) increase of volume at constant pressure, or (b) increase of pressure at constant volume, with temperature. The coefficient of expansion of a gas, or the coefficient of increase of pressure with temperature being large, the effect of the glass bulb is of less relative importance than in a liquid thermometer; but much work has been carried out to provide a satisfactory standard glass for which all the necessary constants are known. The gas thermometer thus becomes the ultimate standard for thermometry, though it is much too troublesome for general use, even as a standard. A carefully-made mercury-in-glass thermometer may be compared directly with a standard gas thermometer, and so become itself a standard from which other mercurial thermometers may be standardised.

It is obvious that comparison with a standard gas thermometer is a standardising operation which may be performed once for all, and may be made either with an arbitrarily selected mercury thermometer, or, if desired, with a thermometer constructed as a standard mercury-in-glass thermometer.

## CHAPTER III

### ELECTRICAL THERMOMETRY AND PYROMETRY

THE electrical resistance of a metal wire varies with temperature in a fairly simple manner, and this variation of resistance affords an accurate means of measuring temperature. Again, the thermoelectric current in a circuit containing two junctions of two different metals depends on the difference of temperature between the junctions, and this variation of current provides a simple means for the measurement of temperature.

The advantage of both these methods lies in their applicability to a very wide range of temperature.

#### 1. The Electrical Resistance Thermometer

This depends on the variation of the electrical resistance of pure metals—chiefly platinum—with temperature. Experiment shows

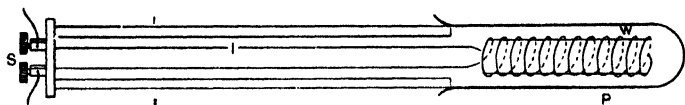


FIG. 18. SIEMENS' PYROMETER.

that the resistance of a piece of pure annealed platinum wire, for example, varies with the temperature, and that, when proper precautions are taken, its resistance is always the same at the same temperature; that is, the repeated heating and cooling of the wire causes no permanent change of resistance. The law of variation of resistance with temperature has been the subject of research by *Matthiessen* and *Siemens*, and later by *Callendar* and *Griffiths*. It is found that the relation  $R_t = R_0(1 + at + bt^2)$ , or even the simpler form—

$$R_t = R_0(1 + at),$$

where  $R_0$ ,  $R_t$  are the resistances of the wire at  $0^\circ \text{C.}$  and  $t^\circ \text{C.}$ , and  $a$  and  $b$  are constants, expresses the variation with fair accuracy. It will be noticed in Chapter IV. that the above relation is similar in form to that used in problems on expansion with change of temperature;  $a$  is called the *coefficient of increase of resistance with temperature*.

The general method of construction of a **platinum resistance thermometer** is illustrated by *Siemens' pyrometer* (Fig. 18). This was one of the first forms of electrical thermometer: its construction is defective in several points, but it was intended for commercial work rather than for accurate scientific work.

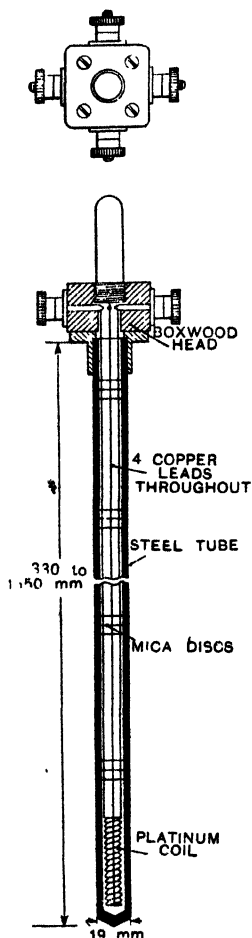


FIG 19.

The platinum wire,  $w$ , is wound on a cylinder of fire-clay and its ends communicate by means of the copper or platinum leads,  $l$ , with the external binding screws at  $S$ . The leads are enclosed in an iron tube,  $i$ , projecting from the wall of the enclosure whose temperature is to be measured; and the wire is protected by a sheath of thin wrought iron, or platinum,  $P$ , fitted on to the "lead" tube, and exposed to the heat of the enclosure. To prevent motion, and to secure insulation, the wire, wound on the fire-clay cylinder, is packed in its sheath with asbestos. The connections for measuring the resistance of the wire are made by means of the screws at  $S$ : this measurement is usually carried out by some form of Wheatstone's bridge. (See Hutchinson's *Elementary Electricity and Magnetism*.)

The chief defect of this form of instrument lies in the fact that the repeated heating and cooling of the platinum wire in contact with fire-clay, and in an iron tube, affect the purity and properties of the platinum to such an extent that the resistance at a given temperature varies considerably.

More recent work shows that, in order to secure constancy of resistance at a given temperature, the wire must be of pure platinum and must be heated in a platinum

or glazed porcelain tube (or for fairly low temperatures in a hard-glass or steel tube), and that for insulation purposes mica is most suitable

The present form of the platinum resistance thermometer is illustrated in Fig. 19. The thin platinum wire, called the "bulb" of the thermometer, is wound on a mica frame and is contained in the lower 4 in. of a protecting steel tube, 1 to 5 ft. long and of 1 in. external diameter. The platinum wire is joined by intermediate short lengths of thicker platinum wire to thick copper leads, which are insulated by passing through holes in discs of mica fitted into the steel tube.

The difficulty due to the fact that these leads are at temperatures different from that of the platinum coil is overcome by inserting a pair of duplicate or compensating leads. These are identical with the other leads and are joined by intermediate pieces of thicker platinum wire to a short length of the same fine platinum wire as used in the "bulb." The four copper wires are joined at the top to the four binding screws fixed in the head, of wood or ebonite, of the instrument. These screws are then joined to a special form of Wheatstone bridge employed for the measurement of the difference of resistance between each pair of leads and the wires connecting them, which depends only on the temperature of the platinum coil. Thus there is no correction for stem exposure when such a thermometer is used.

A very convenient form of the Wheatstone bridge, known as the *Callender-Griffiths bridge*, has been specially devised for temperature measurement with the platinum resistance thermometer (Fig. 20). The upper part of the figure shows the arrangement of a simple form of the bridge, the scheme of connections being shown in the lower part. P and Q are equal resistance coils of 10 ohms. The bridge wire is AB, and the right-hand part of this, together with the platinum wire, T, of the thermometer and its leads, constitute the third arm of the bridge. The left-hand part of the wire, AB, together with the compensating wire, C, and its leads and also a series of coils, R, of known resistance, constitute the fourth arm of the bridge. E is a battery, G a galvanometer, and F a sliding jockey making contact between AB and a second wire, HG<sub>2</sub>, and thus with the galvanometer.

If the bridge is balanced when F is at O, the middle point of AB, then since  $P = Q$ ,

$$T + r + AO = R + r + BO,$$

where  $r$  is the resistance of the thermometer leads and the compensating leads, T the resistance of the thermometer, and R the resistance of the coils used. Since  $AO = OB$ , then  $T = R$ .





R, used. Hence, the resistance of the thermometer at any temperature may be found by balancing the bridge. A vernier attached to the jockey, F, enables bridge readings correct to 0.1 mm. to be made.

Temperature on a platinum thermometer of this kind is defined by Callendar and Griffiths in the following way: Taking the simple relation

$$R_t = R_0 (1 + a \, pt)$$

where  $pt$  is a *platinum thermometer temperature*, then if  $R_{100}$  is the resistance of the wire at the temperature of steam from water boiling under normal pressure,  $R_0$  the resistance at the temperature of melting ice, and  $R_t$  the resistance at any other temperature,  $pt$ , then,

$$pt = \frac{R_t - R_0}{R_{100} - R_0} \times 100.$$

The value of  $R_{100} - R_0$  is called the *fundamental interval* of the thermometer.

Temperatures determined in this way will not correspond with gas thermometer temperatures, but Callendar, and later Griffiths, found that the difference,  $d$ , between the two scales is expressed, for a wide range of temperatures, by the relation

$$d = t - pt = \delta \left\{ \left( \frac{t}{100} \right)^2 - \left( \frac{t}{100} \right) \right\},$$

where  $t$  denotes the gas thermometer temperature on the *Centigrade* scale, and  $\delta$  a constant, known as the *difference coefficient*, depending on the chemical constitution of the platinum wire, which may be determined once for all for any given thermometer. This relation has been shown to be strictly true for temperatures up to  $1000^\circ \text{C}$ .

The value of  $d$  is determined by observation of the resistance of the thermometer at three known temperatures, the points usually selected for this purpose being  $0^\circ \text{C}$ . and  $100^\circ \text{C}$ ., the freezing and boiling points of water respectively, and  $444.5^\circ \text{C}$ ., the temperature of sulphur boiling under normal pressure. The value of the factor,  $\delta$ , may be taken as 1.50 for most samples of platinum wire. Tables can be obtained showing the corrections to be applied to temperatures obtained on the platinum scale in order to give the corresponding gas scale temperatures. If the relation

$$R_t = R_0 (1 + at + bt^2)$$

is used, the values of  $R_t$ , when  $t$  is  $0^\circ \text{C}$ .,  $100^\circ \text{C}$ ., and  $444.5^\circ \text{C}$ .

should be found, and a graph plotted showing the relation between  $R_t$  and  $t$ . A convenient fixed point, higher than the sulphur point, is the temperature of melting potassium sulphate,  $1070^\circ\text{C}$ .

One great advantage of this type of thermometer is that the addition of compensating leads renders the indications of these instruments independent of the depth of immersion of the thermometer in the hot region, so long as the bulb is wholly immersed, and of the distance of the thermometer from the temperature measuring apparatus. Further, apparatus has been designed by *Whipple* to make the Wheatstone bridge indicate temperature *directly*, and this apparatus is so simple that an ordinary workman can use it.

Temperature can be recorded continuously by these thermometers when connected to a Callendar patent recorder. The recorder, actuated by clockwork, balances automatically the resistance of the thermometer, and a pen records the actual temperature on a sheet of paper fixed to a revolving drum.

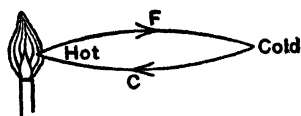


FIG 21.

These thermometers have important and extensive applications in all forms of industry where temperature is an important factor, from cold-storage chambers and hospitals to annealing furnaces and steel casting. Such a

thermometer is one of the most reliable means of measuring temperature, and readings correct to within  $0.1^\circ\text{C}$ . can be taken from  $-40^\circ\text{C}$ . to  $1300^\circ\text{C}$ ., the sensitiveness remaining approximately constant.

## 2. The Thermo-Electric Thermometer

If an electrical circuit is made of wires of two different metals joined together at their ends, and the junctions of the metals are kept at different temperatures, a current is set up in the circuit. Such a current can be produced by heating one of the junctions, or more generally by establishing, in any way, a difference of temperature between the two junctions. The existence of the current can be shown by including a galvanometer in the circuit. The current is maintained so long as the difference in temperature is maintained, and varies in direction and strength as this difference varies. Such junctions are termed *thermo-electric elements or couples*.

Thus, if pieces of iron and copper wire are used in this way (Fig. 21), it can be shown by experiment that, for moderate

temperatures, the current always flows from copper to iron across the hot junction. Similar results are obtained with a couple formed with wires or rods of any two metals, but the direction and magnitude of the currents are different for different metals.

The current is roughly proportional to the difference between the temperatures of the junctions, so that a measurement of the current by a galvanometer serves as a measurement of this difference of temperature. It is not essential that the circuit should consist merely of the two metals and the two junctions. It may be completed through wires of other metals, galvanometers, etc., so long as the junctions of the two metals with the remaining part of the circuit are at the same low temperature. For a moderate difference of temperature, the current is greatest when the metals are antimony and bismuth. Iron and nickel, copper and constantan or eureka, an alloy of copper and nickel, also give currents of the same order of magnitude. The former may be used up to  $300^{\circ}\text{C}$ . and the latter to  $500^{\circ}\text{C}$ . For high temperature work, however, these metals are not sufficiently durable, and for work up to  $1400^{\circ}\text{C}$ . the metals should be platinum and an alloy of platinum with 10 per cent. iridium; and for work up to  $1600^{\circ}\text{C}$ . platinum and an alloy of platinum with 10 per cent. rhodium.

A form of the **thermo-electric thermometer** is illustrated in the diagram (Fig. 22). Two fine wires, of diameter 0.6 mm., of the metals employed are threaded through fine porcelain tubes. At the lower end the wires are welded together, and it is this junction which is exposed to the heat. The wires are placed in a large porcelain tube, and a cap of wood or ebonite carries binding screws which are joined internally to the junction wires and externally to the temperature measuring apparatus. The other junction of the metals should be

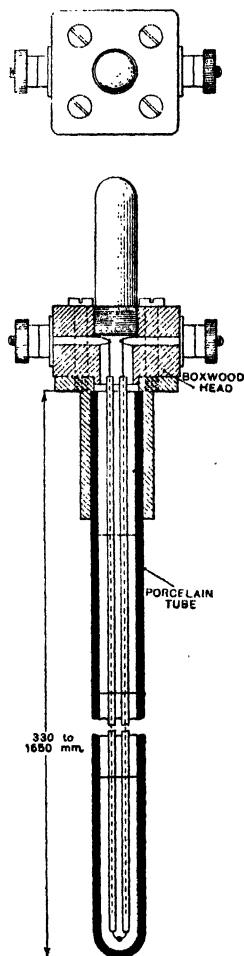


FIG. 22.

kept, for strict accuracy, at a constant low temperature, but since the instrument is employed usually for the measurement of very high temperatures, it is sufficient if the other junctions are kept fairly cool.

It is actually the electromotive force in the circuit which depends on the nature of the metals and the temperatures; the current is simply the quotient of the electromotive force by the resistance of the circuit. For approximate work it may be assumed that the resistance of the circuit does not change and the current is measured by a galvanometer. The error made is lessened if the galvanometer is of such high resistance that the variation of the resistance of the metals composing the hot junction is negligible. For very accurate work, however, the electromotive force should be measured by means of a potentiometer.

The relation between the electromotive force and the temperature is given in textbooks of Magnetism and Electricity.\* It is

$$E \propto (t - t_1) \left( \frac{t + t_1}{2} - t_n \right),$$

where  $E$  is the E.M.F. in the circuit when the low and high temperatures of the junctions are  $t_1^\circ \text{C.}$  and  $t^\circ \text{C.}$ , and the neutral point of the metals is  $t_n$ .

In practice, thermocouples are used only for very high temperatures, and an approximate relation which may be used with the thermocouples usually employed when  $t_1$  is nearly  $0^\circ \text{C.}$  is

$$\log E = A \log t + B,$$

where  $A$  and  $B$  are constants depending on the metals employed. Another relation which is sometimes used is

$$E = P + Qt + Rt^2,$$

where  $P$ ,  $Q$ , and  $R$  are constants. These relations do not quite agree, and, in practice, it is best to standardise each particular thermocouple by finding its E.M.F. at known temperatures.

The E.M.F. generated by the platinum-platinum iridium junction is approximately 15 microvolts per degree C., and that by the platinum-platinum rhodium junction 10 microvolts per degree C. These couples will give temperatures correct to  $1^\circ \text{C.}$  from  $1000^\circ \text{C.}$  up to the melting point of platinum,  $1710^\circ \text{C.}$  For temperatures

\* See Hutchinson, *Advanced Textbook of Electricity and Magnetism*, or the same author's *Intermediate Textbook of Electricity and Magnetism*.

\* below 300° C. a nickel-iron junction, which gives 30 microvolts per degree C. difference between the junction-temperatures may be used.

In commercial work a high resistance galvanometer is used with thermocouples, and it can be made direct reading; and also by a clockwork arrangement to give continuous records. The measuring instrument may be placed at a great distance from the couple, as the resistance of the leads is almost negligible in comparison with that of the galvanometer.

The thermoelectric thermometer will not measure temperature with the accuracy of the resistance thermometer, but it possesses the advantage that it will measure the temperature *at a point*.

### 3. Pyrometry

The measurement of very high and very low temperatures has been attempted in very many ways with varying degrees of success. A summary of the various methods is given—

(1) ELECTRICAL PYROMETRY.—There are, as explained above, two electrical methods by which both high and low temperatures may be measured very accurately, one based on the measurement of the electrical resistance of metals, and the other on the measurement of the thermo-electric effects set up at the junctions of different metals.

(2) CALORIMETRIC METHODS.—One of the oldest methods of measurement is indicated in Qu. 8 of Ex. VII. A calorimetric method of this kind is essentially rough and inaccurate, but it is a convenient method of getting an approximate value of the temperature of a furnace.

(3) THE GAS THERMOMETER.—The most reliable of the earlier pyrometers were modifications of the gas thermometer. On page 108 it is explained that an air thermometer with a porcelain bulb forms a most reliable pyrometer, but, although the air-thermometer method is susceptible of very great accuracy, the experimental work necessary to obtain very accurate results is difficult and troublesome, so that, although valuable as a standard of reference the air thermometer is not convenient for use when a number of individual accurate determinations have to be made.

(4) GAS WEIGHT THERMOMETER.—*Deville and Troost's pyrometer*, described by them in 1860, was a simple air thermometer. It was made of porcelain, and was used to determine the temperature

of a furnace in exactly the same way as the weight thermometer described on page 93, might be supposed to be used to determine the temperature of the steam chamber, assuming the coefficient of expansion of air to be known. In methods of this kind, however, it is evident that the coefficient of expansion of porcelain must be known with some accuracy. The expansion of the bulb affects the accuracy of the indications of both constant pressure and constant volume gas thermometers.

(5) SEGER CONES.—These are small cones made of refractory mixtures of definite melting points. They are exposed on a plate to the heat of a furnace, when some of them will melt and others remain unchanged. After a sufficiently long exposure, the plate is withdrawn and the cones examined, whence the temperature of the furnace may be deduced with some accuracy.

(6) THE VAPOUR PRESSURE THERMOMETER.—The maximum vapour pressure of a liquid depends only on the temperature of the liquid, and a vapour pressure determination may be used to find the temperature. A form of apparatus for this purpose will be described (page 197), in which the expansion of the bulb has no effect on the reading, though the varying temperature of the liquid column is a disadvantage in this type of thermometer.

(7) VAPOUR DENSITY METHODS.—Another convenient method of pyrometry, suggested by *Regnault*, is by means of vapour density determinations. For example, suppose the density of iodine vapour or mercury vapour is known over a range of temperature; a small quantity of iodine, say, may be placed in a porcelain bulb, or flask with a long, fine stem, and the bulb put in the furnace, allowing the end of the stem to protrude slightly. The iodine is vapourised and the vapour fills the bulb at the temperature of the furnace; the end of the stem is then sealed off, and the weight of the iodine remaining in the bulb is determined. The volume of the bulb and the mass of vapour it contains being known, the density of the vapour and, therefore, the temperature of the furnace can be found (page 199).

(8) OPTICAL METHODS.—When a body, such as an iron sphere, is heated gradually in the dark, the first light emitted consists of dull red rays. With further rise of temperature the light changes to bright red. After that, orange rays are added to the red rays and, as the heating proceeds further, there are added in succession

green, blue, and violet rays. The body is now white hot, and further heating has no effect on the colour but only increases the brightness. Thus it is possible to estimate the temperature of an incandescent body, the light emitted being due to heat, by noting carefully its colour. The first colour, dull red, appears at about  $525^{\circ}\text{C}$ . As the body is still heated the colour turns to cherry red at  $800^{\circ}\text{C}$ . and to a full yellow at  $1000^{\circ}\text{C}$ . White appears at  $1300^{\circ}\text{C}$ ., and dazzling white at  $1500^{\circ}\text{C}$ . and above.

Intermediate temperatures may be observed by means of an instrument, the **Optical Pyrometer**, based on the above scheme. In other forms of optical pyrometer, comparison is made between the intensity of the light emitted by the hot body and that emitted by another hot body of known temperature.

(9) **RADIATION METHOD.**—In this method, measurements are made of the total radiation emitted by the hot body whose temperature is required, and the temperature is deduced by the

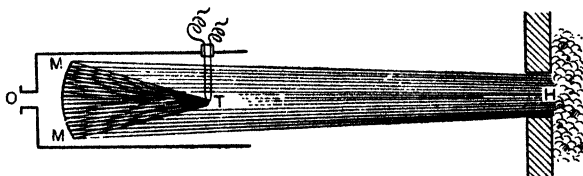


FIG. 23.

application of the known laws of radiation. Further details of radiation methods are given in the next section.

#### 4. Radiation Pyrometers

In all the forms of pyrometer described there is some part which has to be in the region whose temperature is under observation. This disadvantage is overcome in the *Féry radiation pyrometer*, which is used for measuring the temperature of a furnace, or other very hot body.

A hole, H (Fig. 23), is made in the side of the furnace, and the radiation passing through this hole impinges on a concave gilt mirror, MM, set up in a short open tube placed some distance away and sighted on H by observation through a hole, O, behind the mirror. The mirror reflects the radiation to a minute copper-constantan thermocouple, T, arranged as a disc and placed at the conjugate focus to H. The current generated by this thermocouple



is measured by a galvanometer, which may be calibrated to give directly the temperature of the furnace.

The temperature of the thermocouple does not rise above  $100^{\circ}\text{C.}$ , but the instrument can be used to measure very high temperatures. It is not accurate for temperatures below  $600^{\circ}\text{C.}$  It may be used to measure the effective temperature of the sun,  $5600^{\circ}\text{C.}$ , by the simple expedient of pointing the instrument at the sun and reading the galvanometer.

The principle on which the instrument is based is that of Stefan's law (page 349), which states that "*the radiant energy emitted by a fully radiating body is proportional to the fourth power of the absolute temperature of the body.*" If the galvanometer attached to the pyrometer has a uniformly graduated scale, and the absolute temperature,  $T_1$ , corresponding to a reading,  $R_1$ , is known, then the absolute temperature,  $T_2$ , corresponding to a reading,  $R_2$ , is given by

$$T_2 = T_1 \sqrt[4]{\frac{R_2}{R_1}}$$

It is assumed here that the fourth power of the temperature of the cool junction is negligible in comparison with  $T_1^4$  or  $T_2^4$ .

In a simpler form of the F ry radiation pyrometer, the thermocouple,  $T$ , and galvanometer are replaced by a small bimetallic spiral which actuates a long pointer moving over a scale graduated directly to give temperatures. The principle is that of the *Breguet thermometer* (page 58).

With both types of instrument the readings are independent of the distance from the source of heat to the mirror, provided that the image of the source produced by the mirror is larger than the receiving disc  $T$ .

## 5. Low Temperature Measurements

In addition to the electrical methods described, which may be used for the measurement of low temperatures, an alcohol thermometer (the freezing point of alcohol is  $-114.9^{\circ}\text{C.}$ ), graduated by comparison with a standard gas thermometer, may be used as already explained.

In the case of the platinum resistance thermometer, the bulb is contained in a brass tube. A convenient fixed point, necessary for the calibration for low temperature work, is the temperature of liquid oxygen boiling under normal atmospheric pressure, which is  $-182.9^{\circ}\text{C.}$

## CHAPTER IV

### EXPANSION OF SOLIDS

**B**EFORE proceeding to quantitative measurements on the expansion of solids due to heat, it is desirable to examine whether all substances do expand on heating and, if so, whether all have the same expansibility.

(a) Fig. 24 depicts two similar strips of steel and copper riveted together along their whole length. On heating by a Bunsen burner the strip becomes curved with the copper on the convex side, *i.e.* the longer side. This shows that copper expands more than steel.

(b) If the experiment be repeated with strips of ebonite and wood glued together along their whole length it will be found that the ebonite expands more than the wood.

(c) If a piece of copper wire be fused into a glass rod and then be allowed to cool, the glass fractures. The copper contracts more than the glass, thus pulling the glass to which it is stuck away from the rest.

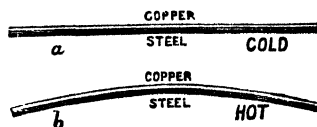


FIG. 24.

(d) On repeating (c) but using a platinum wire no fracture occurs, showing that glass and platinum expand and contract to about the same extent.

The results of many experiments such as the above show that all common substances expand on heating and contract on cooling, the extent of expansion being different for different substances.

#### 1. Linear and Cubical (Volume) Expansion

When an isotropic body—a body which possesses the same properties in all directions, such as metals, liquids, gases—is heated, it in general expands, *and it expands equally in all directions* (a non-isotropic body like a crystal does not). The expansion of isotropic substances only will be dealt with here. For example, if a cube of an isotropic substance is heated, each edge increases equally in length, each face increases equally in area, and the volume of the cube as a whole increases also. Increase of length is

referred to as *linear expansion*, increase in area as *superficial expansion*, and increase of volume as *cubical or volume expansion*.

The study of the amount of expansion may be made by exact measurements of change of length or by exact measurements of change of volume. When length measurements are made linear expansion is determined directly, and the corresponding superficial and cubical expansions may be deduced from the result. When volume measurements are made volume or cubical expansion is determined directly, and the corresponding linear and superficial expansion may be deduced from the result.

## 2. Expansion and Temperature

It must be remembered that the thermometric scale of temperature is derived from the expansion of mercury in a glass tube, and that successive degrees of temperature correspond to successive equal increments of volume. It should be noticed, however, that the increments of volume for successive degrees of temperature are not strictly equal. In constructing a thermometer the volume of the bore of the stem between the fixed points is divided into equal divisions. In using the instrument the volume of each division increases with the expansion of the glass tube as the temperature rises, so that the increment of volume for each successive degree increases slightly, and the increment of volume from  $99^{\circ}\text{C.}$  to  $100^{\circ}\text{C.}$  is therefore greater than that from  $0^{\circ}\text{C.}$  to  $1^{\circ}\text{C.}$  by the increase in volume of a degree division due to the expansion of the glass tube between  $1^{\circ}\text{C.}$  and  $100^{\circ}\text{C.}$  Hence, if the expansion of any body degree by degree is measured and the same expansion for each degree rise of temperature is found, it might be said that the rate of expansion with temperature is uniform, but such a statement would mean merely that *the body expands in exactly the same way as mercury in glass appears to expand*.

It is found that as a general rule substances expand in approximately the same way as mercury in glass. That is, the increment of length or volume for each degree rise of temperature is *approximately* the same, and the expansion for one degree rise of temperature is approximately  $1/n$ th of the expansion for  $n$  degrees rise of temperature.

## 3. Coefficient of Linear Expansion

Experiment shows that if different bodies of the same material are heated through the same range of temperature, a unit length increases in length by *the same fraction* for each degree rise in

temperature. For example, if the temperature of any body made of copper is raised  $1^{\circ}\text{C}$ . (and, practically, at any part of the Centigrade scale) then the increase in length per unit length is found to be about  $\frac{1}{80000}$ . This fraction  $\frac{1}{80000}$  is called the *coefficient of linear expansion* of copper. Thus it may be said that the **coefficient of linear expansion** of the substance composing a body is numerically equal to the change in length per unit length for a rise in temperature of one degree. (But see below.)

Now let the length of a body at a temperature of  $t_1^{\circ}\text{C}$ . be  $L_1$  and at  $t_2^{\circ}\text{C}$ . be  $L_2$ , and let  $l$  be the coefficient of linear expansion. Then:—

Increase of length when heated  $(t_2 - t_1)^{\circ} = L_2 - L_1$ ;

Increase of length when heated  $1^{\circ} = \frac{L_2 - L_1}{t_2 - t_1}$ ;

$\therefore$  Coefficient of linear expansion  $= \frac{L_2 - L_1}{L_1 (t_2 - t_1)}$ ;

$$\text{i.e. } l = \frac{L_2 - L_1}{L_1 (t_2 - t_1)} \dots\dots\dots (1)$$

If, as is the usual case, the preliminary measurements are made at  $0^{\circ}\text{C}$ ., and  $L_0$  is the length of the body at this temperature, and  $L_t$  the length at the temperature of  $t^{\circ}\text{C}$ ., then the above relation becomes

$$l = \frac{L_t - L_0}{L_0 \cdot t} \dots\dots\dots (2)$$

$$\therefore L_t = L_0 (1 + lt) \dots\dots\dots (3)$$

It should be noted that the value of  $l$  given by the relations (1) and (2) is the average or mean coefficient of linear expansion between  $t_1^{\circ}$  and  $t_2^{\circ}$ , or, in the latter case between  $0^{\circ}\text{C}$ . and  $t^{\circ}\text{C}$ . (See Art. 7.)

Since  $(L_t - L_0)/t$  in (2) above is the increase in length for  $1^{\circ}\text{C}$ . rise in temperature, it follows from the formula that the **coefficient of linear expansion** is the ratio

$$\frac{\text{Increase in length for } 1^{\circ}\text{C. rise in temperature}}{\text{Length at } 0^{\circ}\text{C.}}$$

and, strictly, this is the true definition of the coefficient of linear expansion, i.e. the reference should be to  $L_0$ , the length at  $0^{\circ}\text{C}$ ., and not to  $L_t$ , the length at any other starting temperature,  $t^{\circ}\text{C}$ .

Thus the statement that the coefficient of linear expansion of copper is 0.000017 really means that if we had a rod of copper, say at a temperature of 15° C., and we raised its temperature to 16° C. it would increase in length by 0.000017 *of the length of the rod at 0° C.*, and not by 0.000017 of the length of the rod at the starting temperature, 15° C. To be exact then, formula (1) above should be written—

$$l = \frac{L_2 - L_1}{L_0 (t_2 - t_1)}.$$

In experiments and calculations *on solids*, however, it is sufficiently accurate to refer to the length  $L_1$  at the starting temperature  $t_1$ ° C., *i.e.* to assume  $l$  is given by the expression (1) above. (See Art. 7.) The following example will indicate this:—

If a copper rod 50 cm. long at 0° C. be left in a room at a temperature of 15° C. for some time its length will be 50.01275 cm.: if the rod be now heated to 100° C. its length becomes 50.085 cm., so that the increase in length for a rise in temperature of 85° C. is 0.07225 cm. Now if reference is made to the starting length at 15° C. the value of  $l$  is:—

$$\frac{L_{100} - L_{15}}{L_{15} \times 85} = \frac{0.07225}{50.01275 \times 85} = 0.00001699,$$

whilst if reference is made, as strictly should be done, to the length at 0° C. the value of  $l$  is:—

$$\frac{L_{100} - L_{15}}{L_0 \times 85} = \frac{0.07225}{50 \times 85} = 0.000017.$$

Thus the error in referring to  $L_{15}$  instead of to  $L_0$  is only about 1 part in 1700 and therefore negligible in practice.

#### 4. Coefficient of Surface Expansion

A body expands equally in all directions, whether the length, breadth, or thickness is considered. Knowing the increase in length and breadth, the increase in area or surface can be found.

The coefficient of surface expansion is defined similarly to that of linear expansion. Thus *the coefficient of surface expansion is numerically equal to the change in surface per unit surface for a rise in temperature of one degree*; or strictly, the coefficient of surface expansion is the ratio—

$$\frac{\text{Increase in surface for 1° C. rise in temperature.}}{\text{Surface at 0° C.}}$$

Thus if  $S_1$  is the area of the surface of a body at  $t_1$ ° C.,  $S_2$  its area at  $t_2$ ° C., and  $s$  the coefficient of surface expansion, then corresponding to (1) above—

$$s = \frac{S_2 - S_1}{S_1 (t_2 - t_1)}, \text{ or more exactly, } s = \frac{S_2 - S_1}{S_0 (t_2 - t_1)} \dots \dots (4)$$

where  $S_0$  is the area at  $0^\circ \text{C}$ . If the starting temperature be  $0^\circ \text{C}$ . and the temperature be raised to  $t^\circ \text{C}$ . so that the area becomes  $S_t$ , then corresponding to (2) above—

$$s = \frac{S_t - S_0}{S_0 t}, \text{ from which } S_t = S_0 (1 + st) \dots\dots (5)$$

Now consider any portion of the surface in the shape of a square whose side measures  $L_0$  at  $0^\circ \text{C}$ . and  $L_t$  at  $t^\circ \text{C}$ . Then—

$$\text{Increase in area} = L_t^2 - L_0^2 = L_0^2 (1 + lt)^2 - L_0^2,$$

$$\text{i.e. Increase in area when heated } t^\circ \text{C.} = L_0^2 (2lt + l^2 t^2);$$

$$\therefore \text{Increase in area when heated } 1^\circ \text{C.} = L_0^2 (2l + l^2 t);$$

$$\therefore \text{Coefficient of surface expansion} = \frac{L_0^2 (2l + l^2 t)}{L_0^2} = 2l + l^2 t.$$

But for any solid  $l$  is very small, and  $l^2$  is therefore negligible. Hence the coefficient of surface expansion for this square  $= 2l$ . This coefficient determines the rate of expansion for any square of any size which can be drawn anywhere on the surface. Hence the rate of expansion for the whole surface must be the same. Thus *the coefficient of surface expansion is twice the coefficient of linear expansion*. For example, the increase in the surface of a copper body per  $1^\circ \text{C}$ . rise of temperature is  $(2 \times \frac{1}{80000})$ , or  $\frac{1}{40000}$  of its surface at  $0^\circ \text{C}$ .; that is, the coefficient of surface expansion of copper is  $\frac{1}{40000}$ .

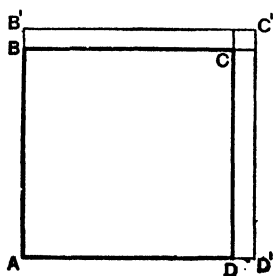


FIG. 25.

The above is capable of a simple geometrical interpretation. Let the square ABCD (Fig. 25) of unit side expand for a rise of temperature of  $1^\circ \text{C}$ . to the square AB'C'D', where  $BB' = DD' = l$ , the coefficient of linear expansion. The increase in area  $=$  the sum of the rectangles B'BC and D'DC, and the square CC'. The square CC' is of almost negligible area compared with the rectangles B'BC and D'DC, and the area of each of these rectangles is  $1 \times l$ . Therefore, the increase in area is approximately  $2l$ , which is thus the coefficient of surface expansion.

Thus, if the coefficient of linear expansion of a substance is known, it is a simple matter to calculate the coefficient of surface expansion. Measurement of surface expansion is not usually made.

### 5. Coefficient of Volume Expansion

This coefficient also is defined similarly to the preceding: thus *the coefficient of volume or cubical expansion of a substance is numerically equal to the change in volume per unit volume for a rise in temperature of one degree, or, strictly, the coefficient of volume (or cubical) expansion is the ratio—*

$$\frac{\text{Increase of volume for } 1^\circ \text{ C. rise in temperature}}{\text{Volume at } 0^\circ \text{ C.}}$$

Thus, if  $V_1$ ,  $V_2$  are the volumes of a body at  $t_1^\circ \text{ C.}$  and  $t_2^\circ \text{ C.}$ , and  $c$  is the coefficient of cubical expansion, then—

$$c = \frac{V_2 - V_1}{V_1 (t_2 - t_1)} \text{ or, more exactly, } c = \frac{V_2 - V_1}{V_0 (t_2 - t_1)} \dots (6)$$

where  $V_0$  is the volume at  $0^\circ \text{ C.}$  If the preliminary measurements are made at  $0^\circ \text{ C.}$  and  $V_t$  be the volume when the temperature is raised to  $t^\circ \text{ C.}$ , then—

$$c = \frac{V_t - V_0}{V_0 t} \dots (7)$$

$$\therefore V_t = V_0 (1 + ct) \dots (8)$$

Next, consider any portion of the volume of a body in the shape of a cube whose side measures  $L_0$  at  $0^\circ \text{ C.}$  and  $L_t$  at  $t^\circ \text{ C.}$  Then (cf. Art. 4) it is found that the coefficient of cubical

expansion for this cube  $= 3l + 3l^2t + l^3t^2 = 3l$  since  $l^2$  and  $l^3$  are negligible. This coefficient determines the rate of expansion of any cube of any size taken anywhere within the volume of the body. Hence the rate of expansion for the whole volume must be the same. Thus *the coefficient of cubical expansion is three times the coefficient of linear expansion.* For example, the increase in volume of a copper body for  $1^\circ \text{ C.}$  rise of temperature is  $(3 \times \frac{1}{80000})$ , or  $\frac{3}{80000}$  of its volume at  $0^\circ \text{ C.}$ , i.e. the coefficient of cubical expansion of copper is  $\frac{1}{80000}$ .

This theorem is also capable of a simple geometrical interpretation. Let the unit cube ABECFDG (Fig. 26) of any material expand to the cube AB'C'D'E' for a rise of temperature of  $1^\circ \text{ C.}$ , the corner A remaining fixed.  $BB' = CC' = DD' = l$ , the coefficient of linear expansion. The increase of volume is made up of

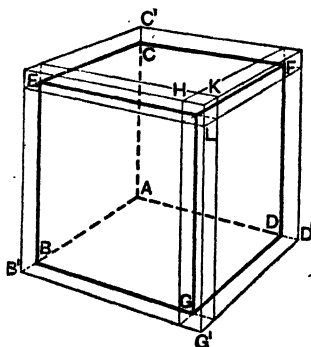


FIG. 26.

three square slabs which stand on the three faces BEG, DFG, CEF of the cube and of height BB', DD', CC' respectively, three square prisms EH, FK, GL, and the corner cube HKL. Since the increase of edge of the cube ABCD is very small, the volumes of the prisms and corner cube are negligible compared with the volumes of the three slabs. The volume of each slab  $1 \times 1 \times l = l$ . Thus the coefficient of cubical expansion is approximately  $3l$ .

It will be seen later that the cubical expansion, and consequently the linear expansion, of a solid substance may be obtained indirectly by observing the expansion of a liquid in a vessel composed of that substance.

## 6. Lengths and Volumes at Different Temperatures

Let  $L_1, L_2$  be the lengths of a rod at  $t_1^\circ \text{C.}$  and  $t_2^\circ \text{C.}$ ,  $t_2$  being greater than  $t_1$ , and let  $l$  be the coefficient of linear expansion of the substance composing the rod. Then for most calculation purposes we may use the relation

$$l = \frac{L_2 - L_1}{L_1(t_2 - t_1)}; \quad \therefore L_2 = L_1\{1 + l(t_2 - t_1)\} \dots\dots\dots (9)$$

a very useful relation when the length  $L_1$  is given at any temperature,  $t_1^\circ \text{C.}$  Similarly, in the case of volume expansion, it will be seen that

$$V_2 = V_1\{1 + c(t_2 - t_1)\} \dots\dots\dots (10)$$

Relations (9) and (10) should not be used, however, when the coefficients of expansion and the differences of temperature are large, although as already indicated scarcely any error is obtained when they are applied to solids. In the case of liquids also, the application of (10) is sufficiently accurate for most purposes.

**Examples.**—In problems on expansion it is better to work from first principles than to calculate mechanically from formulae.

(1) *The length of a copper rod at  $10^\circ \text{C.}$  is  $200\cdot34$  in. Find its length at  $100^\circ \text{C.}$ , the mean coefficient of linear expansion being  $0\cdot000017$ .*

Difference of temperature is  $100 - 10 = 90^\circ \text{C.}$

A unit length at  $10^\circ \text{C.}$  increases by  $90 \times 0\cdot000017$  or  $0\cdot00153$  when heated to  $100^\circ \text{C.}$ ;

$\therefore 200\cdot34$  in. increase by  $200\cdot34 \times 0\cdot00153$ , or  $0\cdot306$  in.;

$\therefore$  length at  $100^\circ \text{C.} = 200\cdot34 + \cdot306 = 200\cdot65$  in.

In working this example it is assumed that the rod expands  $0\cdot000017$  of its length at  $10^\circ \text{C.}$  for each degree increase of temperature. This is not strictly true (see Art. 3). The rod expands  $0\cdot000017$  of its length at  $0^\circ \text{C.}$ , for each degree rise, but no appreciable error is made, since its length at  $10^\circ \text{C.}$  is very nearly the same as at  $0^\circ \text{C.}$



(2) The volume of a piece of glass at  $100^{\circ}\text{C}$ . is  $100.258\text{ c.c.}$ , and its volume at  $0^{\circ}\text{C}$ . is exactly  $100\text{ c.c.}$  Find the mean coefficient of cubical expansion.

$$100.258 - 100 = 0.258\text{ c.c.}$$

The increase in volume for  $100^{\circ}\text{C}$ . is  $0.258\text{ c.c.}$ : hence for  $1^{\circ}\text{C}$ . it is  $\frac{0.258}{100}$   
 $= 0.00258\text{ c.c.}$

$\therefore$  the coefficient of cubical expansion, since the volume at  $0^{\circ}\text{C}$ . is  $100\text{ c.c.}$

$$\text{is } \frac{0.00258}{100} = 0.0000258.$$

The coefficient of linear expansion is  $\frac{1}{3} \times 0.0000258$ , or  $0.0000086$ , and that of surface expansion is  $2 \times 0.0000086$ , or  $0.0000172$ .

(3) The coefficient of linear expansion of glass is  $0.0000083$ . Find the volume at  $15^{\circ}\text{C}$ . of a glass flask of exactly  $1\text{ litre}$  capacity at  $0^{\circ}\text{C}$ .

In dealing with hollow vessels, note that if the space inside was filled exactly with the same matter as that of which the vessel is composed, and the vessel and contents were heated, the matter put in would fill the vessel exactly at all temperatures. But, the volume of the matter put in is equal to the capacity of the vessel, hence the increase of volume of a hollow vessel depends upon the cubical expansion of the substance composing the vessel.

The coefficient of cubical expansion of glass is  $0.0000249$ . The increase in capacity of the flask per degree is  $0.0000249 \times 1000$ , and therefore the increase for  $15^{\circ}\text{C}$ .  $= 0.0000249 \times 1000 \times 15 = 0.37\text{ c.c.}$

$$\therefore \text{Capacity at } 15^{\circ}\text{C} = \frac{1000.37\text{ c.c.}}{1000.37\text{ c.c.}}$$

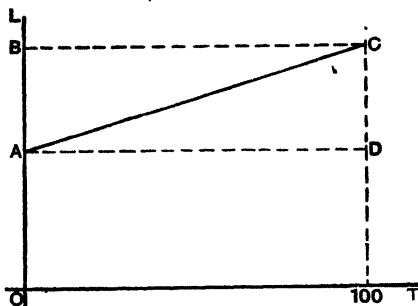


FIG. 27.

## 7. Mean Coefficient of Expansion

The fraction  $\frac{L_2 - L_1}{L_1(t_2 - t_1)}$  has been taken above to be the coefficient of linear expansion between  $t_1^{\circ}$  and  $t_2^{\circ}$ . If the expansion is regular, the coefficient of linear expansion between  $t_1^{\circ}$  and  $t_2^{\circ}$  is the same as the coefficient at all temperatures between  $t_1^{\circ}$  and  $t_2^{\circ}$ . If, however, the expansion is not regular, this quantity must be called the *mean* coefficient of linear expansion between  $t_1^{\circ}$  and  $t_2^{\circ}$ , and if it is wished to determine the *true* coefficient of linear expansion at a particular temperature  $t^{\circ}$ , a different method must be adopted.

Let  $L$  be the length at  $t^{\circ}$  and  $L'$  the length at a temperature  $t'^{\circ}$ , a little above  $t^{\circ}$ . Then the mean coefficient of linear expansion between  $t^{\circ}$  and  $t'^{\circ}$  is evidently  $(L' - L)/L(t' - t)$ . If the difference of temperature  $(t' - t)$  be taken very small, the change of length

also will be very small. Thus, the fraction,  $(L' - L)/L (t' - t)$ , tends to a certain limiting value which is the true coefficient of linear expansion at  $t^\circ$ . Denoting the change of temperature by  $\tau$ , and the change of length by  $L$ , the coefficient becomes  $\frac{1}{L} \cdot \frac{L}{\tau}$ .

Similarly, the true coefficient of cubical expansion at a temperature,  $t$ , is given the expression,  $\frac{1}{V} \cdot \frac{v}{\tau}$ , where  $v$  denotes a very small change of volume and  $\tau$  a very small change of temperature.

Frequently the *small* change in length is denoted by  $dl$  and the *small* change in temperature by  $dt$ , and the above expression for the linear coefficient is written  $\frac{1}{L} \cdot \frac{dl}{dt}$ . Similarly the volume coefficient

is written  $\frac{1}{V} \cdot \frac{dv}{dt}$ .

## 8. Graphical Representation of Expansion

Let OT (Fig. 27) be the axis of temperature and OL the axis of length. Let OA represent the length of a rod at  $0^\circ$  C., and OB the length at  $100^\circ$  C. Then the point C represents the rod at  $100^\circ$  C., and the mean coefficient of linear expansion from  $0^\circ$  C. to  $100^\circ$  C. is  $\frac{OB - OA}{100 \times OA}$ , or  $\frac{1}{100} \cdot \frac{CD}{OA}$ . If the expansion is uniform, that is, the rod increases in length by the same amount for every equal rise of temperature, it is obvious that the graph showing the relation between length and temperature is the straight line AC. The equation of this line is  $L_t = L_0 (1 + lt)$  where  $l = \tan \angle CAD$ ; the value of  $l$  is what has been called the coefficient of linear expansion.

If the expansion is *not* uniform, the graph showing the relation between length and temperature will be curved. The line AC (Fig. 28) represents the case in which the coefficient of linear expansion increases with temperature. The mean coefficient of linear expansion from  $0^\circ$  to  $100^\circ$  C. is  $\frac{1}{100} \cdot \frac{CD}{OA}$  as before.

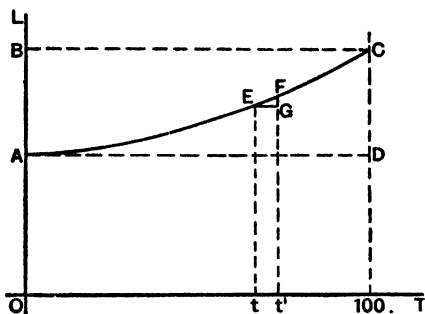


FIG. 28.

To obtain the coefficient of linear expansion at an intermediate temperature,  $t$ , take another temperature,  $t'$ , a little higher than  $t$ , and draw ordinates to cut the graph in E and F. Draw EG perpendicular to Ft'. Then for the small increase of temperature,

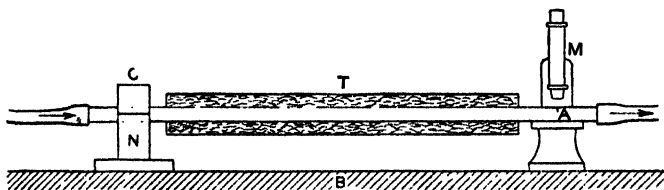


FIG. 29.

$(t' - t)$ , the expansion is FG, and the coefficient of linear expansion at  $t$  is equal to the limiting value of  $\frac{1}{OA} \cdot \frac{FG}{EG}$  when E and F are indefinitely close together. Now the line, EF, is the tangent to the graph at E when E and F are indefinitely close together. Hence the coefficient of linear expansion at  $t^\circ$  C. is

$$\frac{1}{OA} \times (\text{Tangent of the angle the tangent at E makes with OT}).$$

The slope of the graph thus readily affords an indication of the variation of the coefficient of expansion.

### 9. Laboratory Methods of Measuring the Coefficient of Linear Expansion

The expansion of most solid bodies with rise of temperature is so small that delicate means of measurement have to be adopted. In the method usually adopted, either a *microscope* or a *micrometer screw* is used. Microscopes suitable for the purpose must be of low power, *i.e.* the field of view should be of about 2 mm. diameter. One form is provided with an eye-piece scale, the value of whose divisions in millimetres is known. Micrometer screws suitable for the purpose may be of either the screw-gauge type or the spherometer.

**FIRST METHOD.**—*Experiment.* To determine the coefficient of linear expansion of brass.—Take a brass tube not less than 50 cm. in length and of about 5 mm. internal diameter. Near one end file a deep notch, N (Fig. 29), and near the other end scratch a sharp clear line, A. Measure with a millimetre scale the distance

between A and N. Mount the tube horizontally, the notch fitting over a knife-edge on which it can be clamped, and the other end resting on the stage of a microscope so that A can be viewed. Attach india-rubber tubes to the ends of the brass tube and pass a stream of cold water through the tubes. Take the reading of A on the eye-piece scale, and take the temperature of the water as it leaves the tube.

Now pass a current of steam through the tube. Observe, in the microscope, the gradual motion of A outwards from N. When A has come to rest, read its position again. The temperature of the steam may be assumed to be  $100^{\circ}\text{C}$ . To prevent condensation in the tube and the possibility of its temperature not being that of the steam, the tube should be surrounded with a layer of cotton-wool, T. To make sure that the readings are correct, pass cold water again through the tube and see if A returns to its original position.

From the two microscope readings find the distance in centimetres through which A has moved. Divide this by the product of the length, NA, and the difference in temperatures of the cold water and the steam: the coefficient of linear expansion of brass is obtained. Note that the calculation is based on the relation: coefficient = (Increase in length)/(Original length  $\times$  Rise in temperature).

**Example.**—In an experiment, when water at a temperature of  $10^{\circ}\text{C}$ . was passing through the tube, the reading of A was 2.4; when steam at  $100^{\circ}\text{C}$ . was passing, the reading was 43.6. The length of NA was 60 cm., and 1 division of the eye-piece scale was equal to 0.0025 cm.

$$\text{The coefficient of linear expansion} = \frac{(43.6 - 2.4) \times 0.0025}{60 \times 90} = 0.000019.$$

**SECOND METHOD.—Experiment.** To determine the coefficient of linear expansion of brass.—Mount a brass rod, about 60 cm. long, on

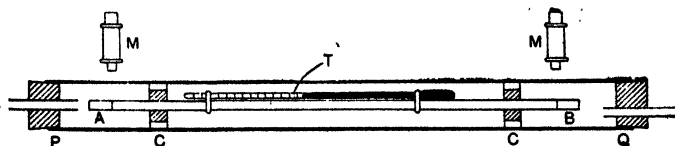


FIG. 30.

corks, CC, and place it inside a glass tube (Fig. 30) through which water and steam can be passed, the corks being cut so that the water and steam may circulate freely. To measure the change of length, use two microscopes, MM, focused on two fine lines, A

and B, near each end of the rod. A thermometer, T, is attached to the rod itself. Pass water and steam through the tube, as in the preceding method. Readings at intermediate temperatures, say  $50^{\circ}\text{C.}$ , may be obtained by passing warm water through the tube. Make quite sure that the temperature, and the positions of A and B, are stationary before reading them. Calculate the coefficient as before. Show from the results obtained that the expansion is proportional to the change of temperature.

**THIRD METHOD.—Experiment.** *To find the coefficient of linear expansion of iron.*—Take an iron tube, as above, close one end by a flat piece of metal, and solder or screw into the tube near it a short tube to act as an outlet. Mount as before, but instead of a microscope use a spherometer. Fix one of the legs of the spherometer in a clamp and arrange the clamp so that the screw can be brought to touch the flat piece of metal, closing the end of the tube. Take readings with cold water and steam and calculate the coefficient as before.

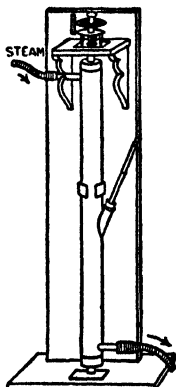


FIG 30 (a).

A simple piece of apparatus based on these "spherometer" methods and suitable for elementary laboratory work of this type is indicated in Fig. 30 (a): the details and methods of using them will be apparent from the figure.

There are many other methods in use; they differ only in the devices which are used to measure the small change of length.

## 10. Historical Methods of Measuring the Coefficient of Linear Expansion

(1) **ROY AND RAMSDEN'S METHOD.**—Roy and Ramsden measured *directly* the expansion of rods by a micrometer screw. This method is interesting as it was devised to determine the true lengths of the metal rods used in measuring the base-line on Hounslow Heath when making the first Ordnance Survey of Great Britain. The pitch of the screw used was  $\frac{1}{80}$  inch, and the head was divided into 100 parts, so that measurements could be made as fine as  $\frac{1}{8000}$  inch.

The method, as slightly modified by later experimenters, is shown *diagrammatically* (Fig. 31). Three troughs are placed parallel

to one another. In each of the two outer troughs is placed a metal rod, AB and EF, and on supports in the middle trough is placed the rod CD, whose coefficient of linear expansion is to be measured. The three rods are approximately of the same length, and near each extremity is fixed vertically a small upright.

The uprights on AB carry cross wires  $a$  and  $b$  (Fig. 32). The uprights on EF carry horizontal rods on which are fixed cross wires,  $e$  and  $g$ , and equal lenses,  $f$  and  $h$ . The upright at the end, C, of CD carries a lens,  $c$ , the upright at the end, D, carries a holder in

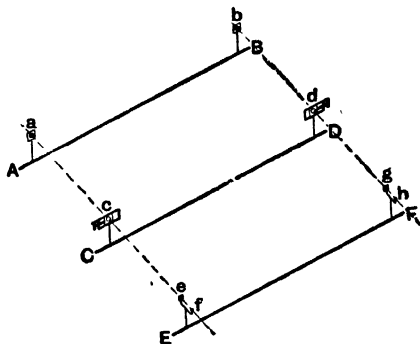


FIG. 31.

which slides a frame (Fig. 33) carrying a lens,  $d$ , exactly equal to  $c$ . The lens frame can be moved parallel to the length of the bar by means of a micrometer screw,  $s$ . The system,  $acef$ , forms a telescope in which an image of  $a$  formed by  $c$  is viewed through  $f$  and its position relative to  $e$  observed. The system,  $bdgh$ , forms an exactly similar telescope.

The three troughs are filled with melting ice, and the rods adjusted until the intersection of the cross wires  $e$  exactly covers the image of the intersection of the cross wires,  $a$ , when seen through  $f$ . Placing the eye at  $h$ , the micrometer screw,  $s$ , is adjusted until the intersection of the cross wires,  $g$ , exactly covers the image of the intersection of the cross wires  $b$ . The reading of the micrometer is then taken.



FIG. 32.



FIG. 33.

The ice in the central trough is melted and the water heated to boiling. The rod, CD, expands, and C moves to the left of the straight line,  $ae$ , and  $d$  to the right of the straight line  $bgh$ . The central trough is moved until  $e$  is brought back into line with  $ae$ , and the micrometer screw,  $s$ , is adjusted again until  $d$  is brought into line with  $bgh$ . The micrometer reading is taken again and the difference between the two readings gives the distance the lens,  $d$ , has been moved to the left, *i.e.* the amount

the length of the rod, CD, between the uprights has expanded on being heated from  $0^{\circ}\text{C.}$  to  $100^{\circ}\text{C.}$  From this the coefficient of linear expansion is obtained.

(2) LAVOISIER AND LAPLACE'S METHOD.—Lavoisier and Laplace magnified the increase in length by mechanical and optical means.

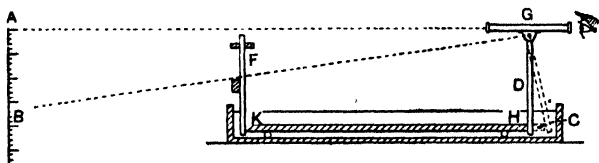


FIG. 34.

The method is shown *diagrammatically* (Fig. 34). A metal rod, HK, is placed in a trough, the end, K, resting against a fixed stop. A lever, D, pivoted at G and carrying a telescope at its upper end, rests against the end H of the rod. The telescope is focused on a scale, AB, fixed vertically some distance away. The trough is filled with melting ice, and the reading on the scale, A, which coincides with the intersection of the cross wires in the telescope, is taken. The ice in the trough is melted and the water heated to boiling. The rod, HK, expands, the end K remaining against the stop and H moves to C. This moves the lever, D, which tilts the telescope, so that the image of the point B on the scale is seen to coincide with the intersection of the cross wires. The reading on the scale is taken. From the similar triangles, ABG, HCG,

$$\frac{AB}{AG} = \frac{HC}{HG}, \text{ or } HC = AB \cdot \frac{HG}{AG}.$$

Thus, if HG and AG are measured, the expansion, HC, can be calculated from the difference, AB, in the scale readings. From this the coefficient of linear expansion is obtained.

(3) THE COMPARATOR METHOD.—This method was designed by the International Bureau of Weights and Measures for the determination of the expansion of the standards of length. It is a much improved form of the method of Roy and Ramsden. A rod of metal rests freely on rollers in a trough (Fig. 35). The trough is double-walled and a steady flow of water is passed through the space between the walls, the temperature being regulated by a thermostat arrangement. The temperature of the water is given by carefully calibrated thermometers, efficient stirrers being

employed to maintain a uniform temperature in the trough. The expansion is measured by two vertical microscopes, A, each fitted with a micrometer eye-piece, mounted on massive stone pillars. Each microscope is focused on a mark near one end of the rod, and its position can be adjusted by means of a micrometer screw, so that the distance between the marks on the rod is obtained. The trough containing the rod is supported on wheels so that it may be moved along rails fixed in a concrete bed. Thus the trough can be run aside and another exactly similar one substituted. In this second trough is placed a standard rod, kept at a constant temperature throughout the experiment. This standard rod is used to indicate whether the distance between the microscopes has varied during the observations.

## II. Anomalies in the Expansion of Solids

(1) If an iron wire is heated gradually, it expands until the temperature is approximately that of dull red heat. It then contracts, and after further heating again expands. Steel behaves in a similar manner. This anomalous contraction occurs at the

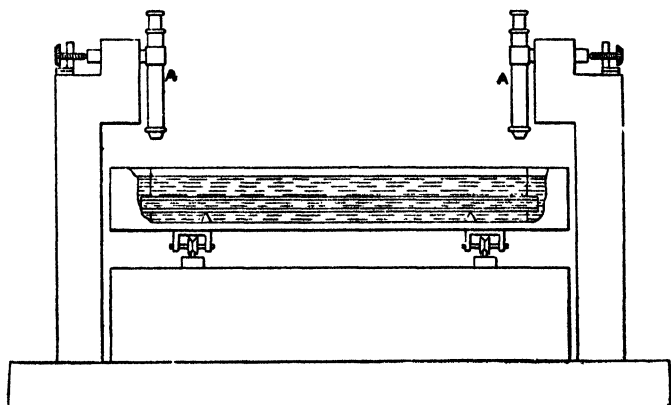


FIG. 35.

temperature at which the material loses its magnetic properties. Evidently at this temperature the molecules undergo some rearrangement.

(2) Joule discovered that, though the coefficient of expansion of vulcanised india-rubber is very large, if a rod of this substance is



stretched the expansion on heating diminishes, and that if the weights used to stretch it are sufficiently heavy it actually contracts when heated. It is sometimes said that the coefficient of expansion of stretched india-rubber is negative. The true explanation is that the elasticity increases on heating, so that a larger force is required to produce the same elongation as at lower temperatures.

(3) Silver iodide contracts when heated, until the temperature of  $116^{\circ}\text{C.}$  is reached. At this temperature the substance changes into an allotropic modification.

(4) Rose's fusible metal, which consists of two parts of bismuth, one part of lead, and one part of tin, expands from  $0^{\circ}\text{C.}$  to  $59^{\circ}\text{C.}$ , and then contracts up to  $96^{\circ}\text{C.}$  when it melts.

(5) Crystals expand differently in different directions; they are not isotropic (Art. 1).

## 12. Cubical Expansion of Solids. Density and Temperature

It will be seen after a study of the Expansion of Liquids (Chapter V.) that the measurement of the cubical expansion of solids involves exactly the same methods as those adopted for the measurement of the cubical expansion of liquids, and that the experimental study of the cubical expansion of solids and liquids is almost one subject.

In the early stages of research into the expansion of solids and liquids, all experimental work on the expansion of liquids was complicated by the expansion of the vessel containing it, and this presented a serious obstacle to the advance of research. The results obtained always involved the coefficients of cubical expansion of a liquid and a solid, and neither could be determined accurately unless the other was known. If the coefficient of absolute expansion of any one liquid or solid were known, this could be taken as a starting point for the determination of other coefficients of expansion.

Attempts were made to obtain a starting point of this kind by making exact determinations of linear expansion, but at that time it was found impossible to make determinations of sufficient accuracy. This difficulty was overcome, however, by the discovery by *Dulong and Petit* of a method of determining the coefficient of absolute expansion of a liquid, and *Regnault's* determination by this method of the coefficient of absolute expansion of mercury gave the starting point of all accurate determinations of the coefficients of cubical expansion of solids and liquids.

In general, when a body is heated it expands, *i.e.* its volume increases, and, since the mass of the body remains constant, it must follow necessarily that its density decreases. For, if  $V_1$  denote the volume at  $t_1^\circ$  and  $V_2$  the volume at  $t_2^\circ$ ; also if  $d_1$  denote the density at  $t_1^\circ$  and  $d_2$  the density at  $t_2^\circ$ , then

$$\text{Mass} = V_1 d_1 = V_2 d_2; \quad \therefore \frac{d_1}{d_2} = \frac{V_2}{V_1}$$

But,  $V_2 = V_1 \{1 + c (t_2 - t_1)\}$  where  $c$  = coefficient of cubical expansion;

$$\therefore \frac{d_1}{d_2} = \frac{V_2}{V_1} = 1 + c (t_2 - t_1) \dots\dots\dots (11)$$

Or, if  $V_0$  denote the volume at  $0^\circ$  C. and  $V_t$  the volume at  $t^\circ$  C.,  $d_0$  the density at  $0^\circ$  C. and  $d_t$  the density at  $t^\circ$  C., in the same manner

$$\frac{d_0}{d_t} = \frac{V_t}{V_0}; \text{ and since } V_t = V_0 (1 + ct);$$

$$\therefore \frac{d_0}{d_t} = 1 + ct, \text{ or } d_t = \frac{d_0}{1 + ct} \dots\dots\dots (12)$$

This last expression is true, as it stands, for solids, liquids, and gases; but for solids and some liquids, *when  $t$  is small*,

$$d_t = \frac{d_0}{1 + ct} = d_0 (1 - ct) \dots\dots\dots (13)$$

The coefficient of cubical expansion of a substance may thus be deduced from the values of its density at different temperatures. This proves of great use in the case of liquids, for the density of a liquid is often more easily ascertainable than its volume.

### 13. Force of Expansion. Precautions on Account of Expansion

The force exerted by a metal rod, if prevented from expanding or contracting as its temperature changes, is very great. For example, if an iron bar of one square inch cross-section is heated from  $0^\circ$  C. to  $100^\circ$  C. and then fixed, so as to prevent contraction, it will exert a force equal to the weight of about 13 tons on the fixings.

This may be illustrated by the simple apparatus shown (Fig. 36). The bar, AB, is held in position in a cast-iron frame, CD, by a short cast-iron rod,  $bb$ , passing through a hole at the end, B, outside the upright, D. The bar is then heated and the screw at the end, A, is tightened. The bar is then allowed to cool and, up to a

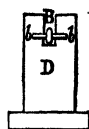
certain point, contraction is resisted by the cast-iron rod; finally, however, the stress becomes too great, and the rod, *bb*, is broken in two.

This contractile force of metals, due to fall of temperature, has many useful applications. The tyres of ordinary carriage and cart wheels are fitted when red hot and, on cooling, bind the wheels firmly together. Boiler plates are riveted with red-hot rivets which, on cooling, draw the plates so close together that a steam-proof joint is formed. In cases where the walls of buildings have bulged outwards, they have been drawn in by passing iron bars through them, across the building, and attaching to their extremities, outside the building, iron plates screwed up to the wall with a nut. The bars are then heated, the nut and plate screwed up tightly against the wall, and the bar allowed to contract, drawing the walls with it. This process is repeated until the walls are made to assume their proper positions.

On the other hand, the expansion of metals is very frequently a source of trouble.



FIG. 36.



Thus, in constructing a railway, small gaps have to be left between the metals to allow for expansion due to the extreme yearly range of temperature. Similarly, allowance must be made for expansion in constructing an iron bridge. For the same reason, the joints of water pipes and gas mains are made like those of a telescope. If furnace bars are fixed firmly they become bent, owing to the expansion which they undergo on heating; for this reason the ends of the bars should be free to move in the direction of their length.

Metal castings often break in cooling, on account of one part cooling more rapidly than another, and thus producing great strains in the metal. For example, in casting a wheel with a thin rim but massive spokes, the rim solidifies and cools much more quickly than the spokes, and as a consequence the contraction of the latter is opposed by the rim, and a strain is set up which may fracture the rim or one or more of the spokes. To avoid this, the spokes are often bent so that they can yield to the strain without breaking.

On account of expansion and contraction, all scales engraved on metal are liable to error if measurements are not made at a

standard temperature. The Imperial Standard Yard is the distance, at 62° F., between two fine lines engraved on gold plugs which are inserted into a bronze bar kept in the Standards Office, and in all measurements made by metal rods or chains, the temperature must be noted and a correction applied.

In the construction of clocks, chronometers, and watches of the better kind, great precaution has to be taken to obviate the effects of expansion on the time-keeping part of the mechanism. The rate of a clock is controlled generally by a pendulum, whose time of vibration varies as the square root of its length, or, more accurately, as the square root of the distance between two points called the *centre of suspension* and the *centre of oscillation* respectively. (See § 93, *Properties of Matter*, Wagstaff.) If the temperature varies this distance varies, and the clock goes *slow* as the temperature rises, and *fast* as the temperature falls. Compensated pendulums are constructed to prevent this change of rate with change of temperature.

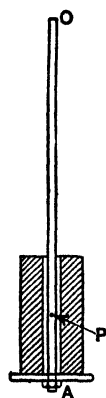


FIG. 37.

**Example.**—The rod of a pendulum is made of light wood, 45 in. long, and supports on a flange at its lower end a heavy metal cylinder, which fits loosely around the rod. What must be the length of the metal cylinder so that the rate of the pendulum may not vary with temperature? The coefficient of linear expansion of the wood is 0.000004 and of the metal 0.00006.

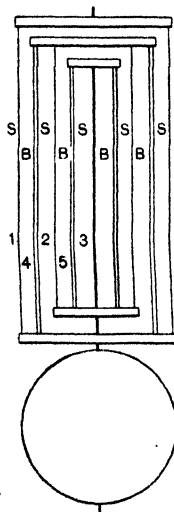


FIG. 38.

The centre of suspension, O (Fig. 37), will be near the upper end of the wooden rod, and the centre of oscillation, P, will be very approximately at the centre of gravity of the metal cylinder. The length of the metal cylinder must be chosen to make the distance, OP, invariable with temperature, *i.e.* if A is the bottom of the rod and cylinder, the length OA of rod must expand just as much as the length, AP, of cylinder.

Thus,  $OA \times \text{coefficient of linear expansion of rod}$

$= AP \times \text{coefficient of linear expansion of metal,}$

$$\therefore 45 \times 0.000004 = AP \times 0.00006,$$

$$\text{or } AP = 3 \text{ in.}$$

The length of the metal cylinder must be, therefore, 6 in.

#### 14. Compensated Pendulum

A pendulum known as *Harrison's grid-iron pendulum* consists of four rectangular frames (Fig. 38), the vertical rods being alternately of steel (S) and brass (B). The central steel rod

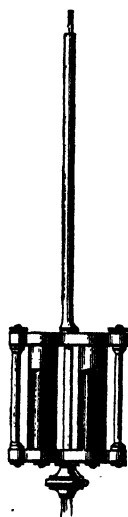


FIG. 39.

passes through holes in the lower horizontal pieces of the frames, and carries the bob at its lower end. The arrangement is such that the steel rods expand downwards while the brass rods expand upwards; and if the downward and upward expansions are equal, the centre of the bob is neither raised nor lowered.

If it were possible to have the total length of each set of rods the same, only one metal would be required. The inner rods must be necessarily shorter than the outer ones, however, and, if compensation is to be exact, they must be made of the more expansive metal. The condition of compensation, therefore, requires that the total expansion of one set of rods should be equal to the total expansion of the other set, the rods being so arranged that these expansions take place in opposite directions. It must be noted here that the two vertical rods of each frame only effect the same expansion of the frame as one rod of the same length, *i.e.* the effective

length of the rods is  $(1 + 2 + 3)$  for steel and  $(4 + 5)$  for brass.

Let  $L_0$  denote the total effective length at  $0^\circ \text{C.}$  of one set of rods, and  $L'_0$  that of the other set. Then:—

$$L_t = L_0 (1 + at) \text{ and } L'_t = L'_0 (1 + a't),$$

where  $a$  and  $a'$  are the corresponding coefficients of linear expansion. Hence, in one case the expansion is given by  $L_t - L_0 = L_0 at$ , and in the other by  $L'_t - L'_0 = L'_0 a't$ . For compensation then:—

$$L_0 at = L'_0 a't;$$

$$\therefore \frac{L_0}{L'_0} = \frac{a'}{a}, \text{ i.e. } \frac{\text{Length of A}}{\text{Length of B}} = \frac{\text{Coefficient of B}}{\text{Coefficient of A}}.$$

The *total effective lengths* of the rods in each set, therefore, must be made inversely proportional to the mean coefficients of linear expansion of the metals of which they are made. For steel and

brass,  $\frac{a'}{a} = \frac{2}{3}$  approximately. In some forms of Harrison's pendulum, *e.g.* that in the clock tower at Westminster, the rods are replaced by concentric tubes. This form is more compact than the open gridiron form.

*Graham's mercurial pendulum* uses the same principle of compensation as that described above. The bob of the pendulum

consists of a frame carrying two glass cylinders containing mercury (Fig. 39). The rod to which the bob is attached expands downwards, while the mercury expands upwards, and if the quantity of mercury is properly adjusted, the final result is that the distance between the centres of suspension and oscillation is unchanged, and the rate of the clock is unaffected, therefore, by changes of temperature. (See Example (3), page 76.)

In chronometers and watches the rate is controlled by balance wheels, which oscillate under the influence of a steel hair-spring. The time of oscillation increases if the dimensions are increased, and a rise of temperature causes the rate to decrease. Further, a rise of temperature lessens the stiffness of the hair-spring, and this also tends to increase the time of oscillation, and diminish the rate. Compensation is effected by making the circumference of the balance-wheel of two metals, the outer being the more expansible. This double rim is made in three parts, each supported by a spoke of the wheel (Fig. 40). The effect of rise of temperature is that, while the end of the segment of the rim nearest the supporting spoke is pushed outwards by the expansion of that spoke, the other end curls in towards the centre of the wheel owing to the greater expansion of the outer strip of metal. By properly adjusting the screw weights carried by each segment, exact compensation can thus be obtained.

In the course of an investigation of the properties of nickel steel, it was discovered by *Guillaume*, a French metallurgist, that the coefficient of expansion of the alloy depends very much on the percentage of nickel. In particular, an alloy containing 36 per cent. of nickel has a coefficient of expansion very nearly zero (see Table II., page 394), whence its name **Invar**. Many of the compensating devices considered above have been rendered obsolete by the discovery of Invar, and it may be used in all cases where the expansion of a metal by rise of temperature introduces complications.

When first discovered, it was thought that Invar would be a suitable alloy from which to construct standards of length. It has been shown, however, that the alloy continues to "grow" for many years after its manufacture, and for this reason it is not used for such standards.

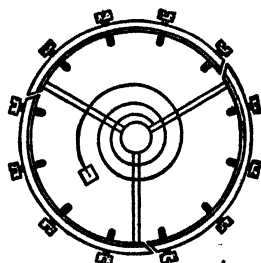


FIG. 40.

On the other hand, Invar has proved very useful for the construction of surveyors' tapes.

### 15. Some Practical Applications of Expansion

The expansion of a body due to heat may be turned to good account. Some automatic fire alarms consist of an electric circuit containing an electric bell. The circuit is not closed at ordinary temperatures, but the break in the circuit is so arranged that, when the temperature rises, an expansion occurs in the metals adjoining the break and contact is made between the two parts of the circuit, the bell then ringing. One type of alarm makes use of a compound strip of brass and iron, so arranged that when it becomes hot it bends (Fig. 24), thus completing the electric circuit.

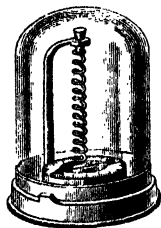


FIG. 41.

In some forms of thermostat, *i.e.* arrangements for maintaining a constant temperature, a metal rod is made to operate a gas supply or an electric switch. When the temperature rises above a certain value, the expansion of the rod causes the supply of heat to be reduced or cut off. On cooling again below this temperature, the supply is restored.

Thermometers based on the expansion of metals have been constructed. They are of little use as accurate instruments, but are convenient for giving an automatic record of the variation of temperature. Two strips of metal of different expansibility are riveted or soldered together and wound into a spiral with the more expansible metal inside. An increase of temperature causes the inner strip to expand more than the outer, and consequently the spiral unwinds. Similarly, if the temperature falls, the spiral coils up. A well known instrument of this type is **Breguet's thermometer** (Fig. 41). It consists of a spiral composed of three metallic strips, of silver, gold, and platinum, soldered together so as to form a single ribbon. The silver, which is the most expansible, is placed inside, the platinum outside, and the gold serves to connect them. The spiral carries at its lower end a horizontal pointer which traverses a dial. As the spiral winds or unwinds with change of temperature, the pointer is deflected in a corresponding direction and thus indicates the variation of temperature.

This form of thermometer is employed in the common forms of recording thermometers or thermographs.

## CHAPTER V

### EXPANSION OF LIQUIDS

SINCE a mass of liquid or of gas has no inherent shape but always takes up the shape of the vessel containing it, it cannot be said that a liquid or a gas possesses a linear or superficial expansion. Volume or cubical expansion only can be dealt with. And it is this expansion which is called *the* expansion of the liquid or the gas.

It is of interest to determine in the first place whether, as in the case of solids, different liquids differ in expansibility: this may be decided by a simple experiment. Fig. 42 depicts three flasks fitted with vertical tubes and containing the liquids indicated, the liquids originally being at the same height in each tube. The three are then immersed as shown in a vessel of warm water. The levels may sink a little at first owing to the expansion of the glass, and then they begin to rise, showing the liquids are more expansible than glass. The rise is different for each liquid—the alcohol expands most and the water least.

It may be mentioned here that *water* has a peculiar property. If ice-cold water (at  $0^{\circ}\text{C}.$ ) be gradually heated, it *contracts* until its temperature reaches about  $4^{\circ}\text{C}.$  and then it expands: but this is dealt with later.

#### 1. Real and Apparent Expansion

When the expansion of a liquid in a graduated containing vessel is observed, the expansion which is *apparent*, or which may be observed, is the combined result of the *real* expansion of the liquid and the expansion of the containing vessel. If the liquid is more expansible than the material of the vessel, it *appears* to expand, but if the liquid is less expansible than the material of the vessel (as in the case of water between  $4^{\circ}\text{C}.$  and  $6^{\circ}\text{C}.$  in a glass vessel) it *appears* to contract. Further, if it were possible to find a liquid which expanded equally with the material of the vessel, there would be no apparent expansion. The expansion of a liquid indicated or made *apparent*

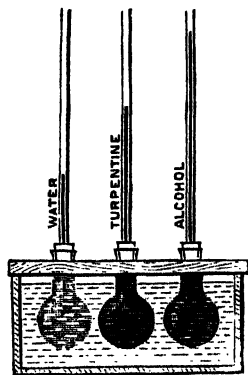


FIG. 42.



in a vessel initially graduated in equal divisions is known as the *apparent expansion* of the liquid in that vessel.

In this connection, reference may again be made to the mercury in glass thermometer: the graduation of the thermometer is based upon the apparent expansion of mercury in glass. The degree divisions of the stem bore are all equal in volume *when the stem is all at one temperature*, but if the thermometer is heated from  $0^{\circ}\text{C}$ . to  $100^{\circ}\text{C}$ . the expansions for each degree rise of temperature, although *apparently* equal, really increase as the temperature rises.

As the thermometer is heated, say, from  $0^{\circ}\text{C}$ . to  $1^{\circ}\text{C}$ ., the mercury must first expand so as to fill up the increase in the volume of the bulb and stem up to the  $0^{\circ}\text{C}$ . mark due to this rise of temperature, and then fill the degree division between the  $0^{\circ}\text{C}$ . and  $1^{\circ}\text{C}$ . marks at a temperature of  $1^{\circ}\text{C}$ . When the thermometer is heated, say, from  $20^{\circ}\text{C}$ . to  $21^{\circ}\text{C}$ ., the mercury must first expand so as to fill the increase in the volume of the bulb and stem, not merely up to the  $0^{\circ}\text{C}$ . mark, but up to the  $20^{\circ}\text{C}$ . mark for  $1^{\circ}$  rise of temperature, and then fill the degree division between the  $20^{\circ}\text{C}$ . and  $21^{\circ}\text{C}$ . marks, not at a temperature of  $1^{\circ}\text{C}$ . but at a temperature of  $21^{\circ}\text{C}$ . The real expansion corresponding to the degree rise of temperature from  $20^{\circ}\text{C}$ . to  $21^{\circ}\text{C}$ . is therefore greater than that corresponding to the degree rise of temperature from  $0^{\circ}\text{C}$ . to  $1^{\circ}\text{C}$ .

If, however, the volume of the bulb is large compared with that of the graduated stem, it may be assumed that the mercury has to expand the same amount per degree rise of temperature; that is, that the scale of temperature depends upon the apparent expansion of mercury in a glass vessel, and other liquids are said to expand uniformly or not according as their apparent expansions in glass vessels are exactly proportional to those of mercury.

Later work has shown that it is preferable to take the standards of temperature from a gas thermometer (see page 103), but since the expansion of mercury in a glass vessel is at all ordinary temperatures very nearly proportional to the expansion of a gas, such as hydrogen, in a vessel of the same glass, no harm results in adhering to the scale of temperature of a mercury thermometer in ordinary work.

## 2. Coefficients of Real and Apparent Expansion

It was shown above that when a liquid contained in a vessel was heated the observed or *apparent* expansion was less than the

*real* expansion. The coefficient of apparent expansion of a liquid in a vessel is given by the ratio

$$\frac{\text{Apparent increase in volume for } 1^\circ \text{ C. rise in temperature}}{\text{Volume at } 0^\circ \text{ C.}}$$

and the coefficient of *real* expansion of the liquid is given by the ratio

$$\frac{\text{Real increase in volume for } 1^\circ \text{ C. rise in temperature}}{\text{Volume at } 0^\circ \text{ C.}}$$

and, of course, the apparent coefficient is less than the real coefficient.

Compare these definitions with those given in Chapter IV. Further, corresponding to the relations given on pages 39, 42, we have, for liquids:—

$$V_a = V_0 (1 + c_a t) \quad \text{and} \quad c_a = \frac{V_a - V_0}{V_0 t}$$

where  $V_0$  = volume at  $0^\circ \text{ C.}$ ,  $V_a$  = *apparent* volume at  $t^\circ \text{ C.}$ , and  $c_a$  = coefficient of *apparent* expansion of the liquid. Further, we have

$$V_t = V_0 (1 + c_r t) \quad \text{and} \quad c_r = \frac{V_t - V_0}{V_0 t}$$

where  $V_t$  = *real* volume at  $t^\circ \text{ C.}$ , and  $c_r$  = coefficient of *real* expansion of the liquid.

To find the relation between the coefficients of real and apparent expansion of a liquid and the expansion of the material composing the vessel, consider the case of a liquid contained in a glass vessel graduated at  $0^\circ \text{ C.}$ , *i.e.* the volumes indicated by the graduations are correct at  $0^\circ \text{ C.}$  Let  $V_0$  be the volume of liquid at  $0^\circ \text{ C.}$ ,  $V_a$  the indicated volume at  $t^\circ \text{ C.}$ , and  $V_t$  the true volume at this temperature. Let  $c_a$ ,  $c_r$  be the coefficients of apparent and real expansion of the liquid, and  $g$  the coefficient of cubical expansion of the material of the vessel.

The real expansion of the liquid = the product of the volume at  $0^\circ \text{ C.}$ , the coefficient of real expansion, and the change of temperature, *i.e.*  $V_t - V_0 = V_0 c_r t$ .

Similarly, the apparent expansion of the liquid is given by  $V_a - V_0 = V_0 c_a t$ .

The difference between them is the volume which a volume  $V_a$  of glass at  $0^\circ \text{ C.}$  has expanded in being heated to  $t^\circ \text{ C.}$ , *i.e.*  $V_a g t$ ;

$$\therefore V_0 c_r t - V_0 c_a t = V_a g t = V_0 (1 + c_a t) g t.$$

Dividing throughout by  $V_0 t$ , we get:—

$$c_r - c_a = (1 + c_a t) g.$$

Neglecting  $c_a t$ , which is usually very small compared with unity,

$$c_r - c_a = g \quad \text{or} \quad c_r = c_a + g;$$

$\therefore$  Real coeff. = Apparent coeff. + Coeff. (cubical) of vessel.

Thus, *the mean coefficient of real expansion of a liquid is approximately equal to the sum of the mean coefficient of apparent expansion of the liquid in any vessel and the mean coefficient of cubical expansion of the material of that vessel.*

The above is applicable also to linear expansion, e.g. the measurement of the linear expansion of a brass rod by means of a steel scale.

It is a simple matter to find the coefficient of apparent expansion of a liquid, but not so easy to find directly that of real expansion. The coefficient of real expansion of mercury, however, has been measured very accurately in classical experiments by *Dulong and Petit*, *Regnault*, and *Callendar and Moss* (Art. 6). Assuming the result (0.0001815) thus found for the range of temperature from  $0^\circ \text{C.}$  to  $100^\circ \text{C.}$  and finding the coefficient of apparent expansion of mercury in a glass vessel, the coefficient of cubical expansion of the material of the vessel can be deduced. Then, if the coefficient of apparent expansion of any other liquid in the same vessel is measured, by using the above relation, the coefficient of real expansion of the liquid can be calculated.

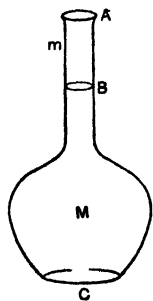


FIG. 43.

### 3. Determination of the Coefficient of Apparent Expansion

There are three easy methods of finding the coefficient of apparent expansion of a liquid, and these will now be described.

(1) **THE WEIGHT THERMOMETER METHOD.**—(a) *Principle of the method.* If a flask full of liquid at  $0^\circ \text{C.}$  is heated to  $t^\circ \text{C.}$ , some of the liquid overflows. Suppose  $m$  grm. overflow and  $M$  grm. remain. Then, at  $0^\circ \text{C.}$  there were  $(M + m)$  grm. in the flask (Fig. 43), say  $M$  grm. below the mark, B, and  $m$  grm. above it.

To find the coefficient of apparent expansion of the liquid, it is assumed that the capacity of the flask does not change with temperature. Then, if  $V_0$  is the volume of  $M$  grm. of the liquid at  $0^\circ \text{C.}$  and  $V_t$  the apparent volume of  $M$  grm. of the liquid at  $t^\circ \text{C.}$ ,  $V_0$  is the volume of the flask to the mark B, and  $V_t$  is the total volume to the mark A. Hence—

$$\frac{V_t}{V_0} = \frac{M + m}{M} \quad \text{or} \quad \frac{V_t - V_0}{V_0} = \frac{m}{M}$$

$$\text{Now, } c_a = \frac{V_t - V_0}{V_0 t}; \quad \therefore c_a = \frac{m}{M t}$$

$$c_a = \frac{\text{Mass of liquid expelled}}{\text{Mass left in at higher temperature} \times \text{Change in temperature}}$$

This relation is also very nearly true when the lower temperature is not  $0^\circ \text{C.}$ , provided that  $t$  represents the actual change of temperature. If greater accuracy is desired, let  $t_1^\circ \text{C.}$  and  $t_2^\circ \text{C.}$  denote the lower and upper temperatures. Then—

$$\frac{1 + c_a t_2}{1 + c_a t_1} = \frac{M + m}{M}; \quad \therefore c_a = \frac{m}{M(t_2 - t_1) - m t_1}$$

The term  $m t_1$  is usually very small compared with  $M(t_2 - t_1)$ , so that—

$$c_a = \frac{m}{M(t_2 - t_1)} \text{ approximately.}$$

**(b) Experiment.**—To find the coefficient of apparent expansion of mercury. A weight thermometer consists of a glass cylindrical bulb (Fig. 44) about 3 in. long and  $\frac{1}{2}$  in. internal diameter, with a stem bent as shown. The stem should have a fine bore, but should be strong enough to bear the weight of the thermometer when full of mercury. Weigh such a vessel. Placing all the apparatus on a mercury tray, support the vessel with the neck dipping under some clean and dry mercury contained in a small dish. Fill the vessel by alternately heating and cooling, keeping the mercury in the dish hot to prevent breakage of the bulb.



FIG. 44.

Place the vessel, with its neck still dipping under mercury, in a balance case with a Centigrade thermometer beside it. Leave for 15 minutes and then read the temperature  $t$ . Hanging the vessel upon the hook of the balance, weigh it, taking care that no mercury escapes through the opening in the meanwhile.

Now place the vessel in a beaker of water so that only the narrow stem projects outside. Heat the water to boiling and keep it boiling for 10 minutes. Collect the mercury which escapes from the opening. Remove the vessel carefully, wipe it and cool it, taking care that no water enters the narrow stem as the mercury contracts on cooling.

Weigh again. From the three weighings find  $M$ , the mass of mercury left in the vessel after heating to  $100^\circ \text{C.}$ , and  $m$ , the mass of mercury expelled during the heating from  $t^\circ \text{C.}$  to  $100^\circ \text{C.}$  Then

$$c_a = \frac{m}{M(100 - t)}$$

The mercury may be removed from the vessel and the experiment repeated with other liquids.

**Example.**—A weight thermometer weighed 5.913 grm. when empty, 61.755 grm. when full of mercury at  $12^\circ \text{C.}$ , 61.022 grm. when full at  $100^\circ \text{C.}$  Find the coefficient of apparent expansion of mercury in glass and hence the coefficient of linear expansion of the glass.

$$m = 61.755 - 61.022 = 0.733 \text{ grm.}$$

$$M = 61.022 - 5.913 = 55.109 \text{ grm.}; t = 12^\circ \text{C.};$$

$$\therefore c_a = \frac{m}{M(100 - t)} = \frac{0.733}{55.109 \times 88} = 0.000151.$$

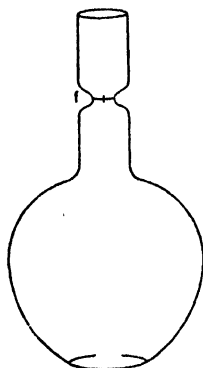


FIG. 45.

Regnault found that the coefficient of real expansion of mercury is 0.000181. Hence, the coefficient of cubical expansion  $g$  of the glass of the weight thermometer is:—

$$g = c_r - c_a = 0.000181 - 0.000151 = 0.000030.$$

Hence, the coefficient of linear expansion of the glass,  
 $l = 0.000010.$

Instead of weighing the vessel full of mercury before heating, the mercury that escapes may be collected in a small beaker and weighed separately. A more accurate value of  $m$  may be obtained by weighing such a small mass than if  $m$  is obtained as a difference of two large masses. If this is done, the experiment may be started from  $0^\circ \text{C.}$  Now:—

$$c_a = \frac{m}{M(t_2 - t_1)}; \therefore t_2 - t_1 = \frac{m}{Mc_a}.$$

Hence, if  $c_a$  is known, the experiment described above could be employed to determine the higher temperature, the lower one being known. The weight thermometer can thus be used as a true thermometer; as such it has the great disadvantage that a weighing is necessary for each individual temperature. It may be used conveniently, however, as a maximum thermometer, for the value of  $t_2$  given by the above relation always represents the maximum temperature experienced.

Other forms of the weight thermometer are the specific gravity bottle (Fig. 45) and the pyknometer (Fig. 46). These can be bought cheaply and have the merit of being easily cleaned and filled.

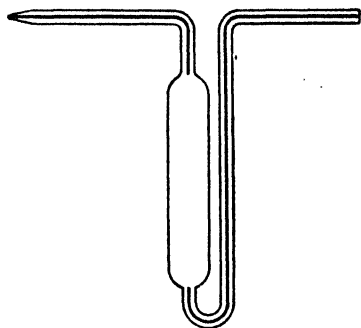


FIG. 46.

## 2) THE VOLUME DILATOMETER

OR THERMOMETRIC METHOD.—

(a) *Principle of the method.* A glass bulb has a long narrow stem of very uniform bore. The volume of the bulb and the area of cross-section of the stem are found. The stem can then be graduated and the volume ascertained up to any graduation mark. The bulb and part of the stem are filled with a liquid and the volume of the liquid at 0° C. is found. The dilatometer is then placed in a bath and its temperature raised. The temperatures at which the liquid column in the stem reaches the various graduation marks are observed. The increases of volume can thus be calculated, and finally—

$$c_a = \frac{\text{Increase of volume}}{\text{Volume at } 0^\circ \text{ C.} \times \text{Change of temperature}}$$

The method is very suitable for liquids which evaporate readily.

(b) *Experiment.*—To find the coefficient of expansion of water at various temperatures. Blow a bulb about 2 in. in diameter on a piece of capillary tubing of  $\frac{1}{16}$  in. bore and about 20 in. long (Fig. 47). Make file marks along the stem at regular intervals. Measure the distances between the first and succeeding marks, using a finely-divided scale or a vernier microscope. Weigh the dilatometer. Warm the bulb slightly, immerse the end of the stem in mercury, and allow a thread of mercury about 6 in. long to enter the stem. Measure the length of the thread accurately. Again weigh the dilatometer. Divide the increase of weight by the density of mercury at the temperature of the observations, to find the volume of mercury. This volume divided by the length of the thread gives the mean area of cross-section of the portion of the stem occupied by the mercury at the temperature of the observations. If the bore of the



FIG. 47.

stem is uniform, the length of the mercury thread will be the same at different parts of the stem.

Remove the mercury by warming the bulb and then fill the bulb with well-boiled distilled water. Adjust the volume of water so that, when the bulb is immersed in ice-cold water at  $0^{\circ}\text{C}.$ , the water column stands in the stem just below the first graduation mark nearest the bulb. Clean and dry the outside, and weigh. The weight of water in grammes thus found may be taken as the volume of water in c.c. at the freezing point,  $0^{\circ}\text{C}.$  Immerse the bulb in a large beaker of water. Stirring well, adjust the temperature so that the liquid surface remains at the first mark on the stem for several minutes. Read the temperature, using a good thermometer.

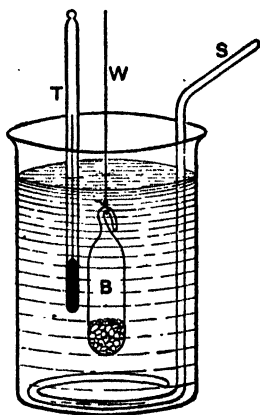


FIG. 48.

Heat the water in the beaker gently until the second mark on the stem is reached. Repeat for succeeding marks up to a temperature of about  $95^{\circ}\text{C}.$

Tabulate results; plot stem graduations against temperatures and draw a smooth curve through the points. It will be seen that the graph is not a straight line, but is concave upwards, showing that the coefficient of expansion is greater for higher temperatures. From the graph, find the mean expansion per degree from  $25^{\circ}$  to  $30^{\circ}$ ,  $30^{\circ}$  to  $35^{\circ}$ , etc., and then the coefficient of expansion between these temperatures.

**Example.**—A volume dilatometer whose stem is uniformly graduated contains water. At  $0^{\circ}\text{C}.$  the level was at the 6th division. When heated to  $10^{\circ}\text{C}.$  it stood at the 7th division, and when heated to  $20^{\circ}\text{C}.$  at the 12th division. A thread of mercury occupying 24 stem divisions weighed 0.072 gm., and the quantity occupying the bulb and stem up to the zero division weighed 12.24 gm. Find the mean coefficient of expansion of water between  $10^{\circ}\text{C}.$  and  $20^{\circ}\text{C}.$

The ratio of the volume of the space between two stem graduations to the volume of liquid at  $0^{\circ}\text{C}.$  is 0.003 to 12.24, i.e. 1 to 4080. The volume at  $0^{\circ}\text{C}.$  is therefore 4086, the volume at  $10^{\circ}\text{C}.$  4087, and the volume at  $20^{\circ}\text{C}.$  4092, i.e. the expansion between  $10^{\circ}\text{C}.$  and  $20^{\circ}\text{C}.$  is 5 divisions. The mean coefficient of apparent expansion between  $10^{\circ}\text{C}.$  and  $20^{\circ}\text{C}.$  is therefore given by—

$$\frac{4092 - 4087}{4086 \times 10} = \frac{1}{8172} = 0.000122.$$

Taking the coefficient of cubical expansion of glass as 0.000026, the coefficient of real expansion of water between  $10^{\circ}\text{C}.$  and  $20^{\circ}\text{C}.$  is thus  $0.000122 + 0.000026 = 0.000148$ .

*Constant volume dilatometers* have been devised in which the volume of the bulb is kept constant by introducing into it a quantity of mercury such that the expansion of the mercury is equal to the expansion of the glass bulb. The ratio of the coefficient of real expansion of mercury to that of glass being  $\frac{0.000181}{0.00026}$  or  $\frac{7}{1}$ , it is evident that if *one-seventh* of the bulb is filled with mercury, the condition of constant volume is attained very approximately.

(3) THE HYDROSTATIC METHOD.—(a) *Principle of the method.* If a body of density  $D$  weighs  $m_1$  grm. in air, and  $m_2$  grm. in a liquid of density  $d$ , it is known that

$$\frac{m_1}{m_1 - m_2} d = D, \quad \text{or} \quad \frac{m_1}{m_1 - m_2} = \frac{D}{d}.$$

If therefore a body of invariable density  $D$  is weighed in a liquid at various temperatures, the variations of  $d$  can be found from the variations of  $(m_1 - m_2)$ . Replacing the quantity,  $(m_1 - m_2)$ , that is, the loss of weight, by  $w$ , then  $w/d = a$  constant, or  $w_1/d_1 = w_2/d_2$ , where  $w_1$  and  $w_2$  are the losses of weight at temperatures,  $t_1^\circ$  and  $t_2^\circ$ , when the liquid has densities  $d_1$  and  $d_2$ . But—

$$d_2 = \frac{d_1}{1 + c(t_2 - t_1)}; \quad \therefore \frac{w_1}{w_2} = 1 + c(t_2 - t_1).$$

In this expression, since the density of the solid body is assumed to be constant,  $c$  is the coefficient of apparent expansion of the liquid, and therefore—

$$c_a = \frac{w_1 - w_2}{w_2(t_2 - t_1)}.$$

(b) *Experiment. To find the apparent coefficient of expansion of a liquid by the hydrostatic method.*—Take a piece of glass tubing about 1 in. in diameter, draw out one end and round it off. Place in the tube enough lead shot or mercury to make the bulb when completed sink in the liquid whose coefficient of expansion is to be determined. Draw off the other end of the tube and bend into a hook to serve as an attachment (Fig. 48).

Then suspend the bulb from one arm of a balance by means of a long thread or fine wire passing through a hole in the base of the balance case, so that the bulb is below the case. The scale pan must be removed and the balance mounted on a suitable support. Counterpoise the bulb by weights placed in the other scale pan. Now arrange a large beaker of the liquid so that the bulb is



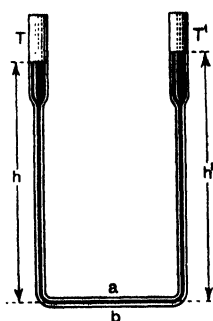


FIG. 49.

completely immersed in the liquid. Leave for some minutes, stirring the liquid gently all the time, and again counterpoise. Thus the loss of weight at the particular temperature of the liquid is obtained. Repeat at two or three other temperatures after heating the liquid.

It is best to start with hot liquid and take observations as the liquid cools. The cooling may be checked at the required temperatures by adding small quantities of hot liquid, stirring well. Then counterpoise so that the bulb is slightly heavier, and with the balance arm free take the temperature when exact balance occurs. From the readings the apparent coefficient of expansion of the liquid over several ranges of temperature can be obtained.

**Example.**—The loss of weight of a glass bulb immersed in water at  $4^{\circ}\text{C}$ . was 23.26 grm., at  $74^{\circ}\text{C}$ . it was 22.74 grm. Find the mean coefficient of apparent expansion of water between  $4^{\circ}\text{C}$ . and  $74^{\circ}\text{C}$ .

$$\frac{\text{Apparent density of water at } 4^{\circ}\text{C.}}{\text{Apparent density of water at } 74^{\circ}\text{C.}} = \frac{23.26}{22.74}$$

Hence, if  $c_a$  is the mean coefficient of apparent expansion of water between  $4^{\circ}\text{C}$ . and  $74^{\circ}\text{C}$ .

$$1 + 70c_a = \frac{23.26}{22.74} = 1 + \frac{0.52}{22.74};$$

$$\therefore c_a = \frac{0.52}{70 \times 22.74} = 0.000327.$$

Matthiessen performed a large number of experiments by this method and used it to determine the coefficient of expansion of water at different temperatures. To obtain the coefficient of real expansion of the water it is of course necessary to know the coefficient of cubical expansion of the solid used. Matthiessen used a glass sinker, and obtained its expansion by first determining its coefficient of linear expansion, thence deducing that of cubical expansion.

#### 4. Determination of the Coefficient of Real Expansion of Mercury

The methods adopted for the determination of this coefficient were all based on the same principle and differed only in experimental detail.

The principle of the methods is simple. If two vertical tubes, communicating by a horizontal branch, each contain a liquid of

given density, the junction of the two liquids being in the horizontal branch, then, for equilibrium, the pressures due to the liquid columns on each side of a cross-section, taken anywhere in the horizontal branch, must be equal.

Thus, consider the pressures on the cross-section at  $ab$  (Fig. 49). Let  $h$  and  $h'$  denote the depth of the centre of gravity of the section below the surfaces of the liquid in  $T$  and  $T'$  respectively. Then, from hydrostatical principles, the pressure on  $ab$  due to the column in  $T$  is given by  $hdg$ , and that due to the column in  $T'$  by  $h'd'g$  (see § 211, *Properties of Matter*, Wagstaff), where  $d$  and  $d'$  are the densities of the liquids in  $T$  and  $T'$  respectively, and  $g$  the acceleration due to gravity. But, since  $ab$  is in equilibrium,

$$hdg = h'd'g; \quad \therefore hd = h'd'.$$

It is evident that this is true whatever shape  $ab$  may have, and whatever may be the shape and size of  $T$  and  $T'$ . If the tubes contain mercury and one column,  $T$ , be kept at  $0^\circ \text{C.}$ , while the other,  $T'$ , is raised to a temperature,  $t^\circ \text{C.}$ , then

$$h_0 d_0 = h_t d_t, \quad \text{or} \quad \frac{h_t}{h_0} = \frac{d_0}{d_t}.$$

$$\text{But } \frac{d_0}{d_t} = 1 + c_r t; \quad \therefore \frac{h_t}{h_0} = 1 + c_r t;$$

$$\therefore c_r = \frac{h_t - h_0}{h_0 t}.$$

Thus the mean coefficient of real expansion of the liquid can be determined by noting  $(h_t - h_0)$ ,  $h_0$  and  $t$ , and the result is independent of the expansion of the tubes containing the liquid.

This method was first used by Dulong and Petit. The tube  $T$  (Fig. 50) was enclosed in a cylinder  $B$ , and surrounded with melting ice. The tube  $T'$  was placed in a thick copper cylinder  $C$  which was filled with oil and, for the purpose of heating it, a furnace was built

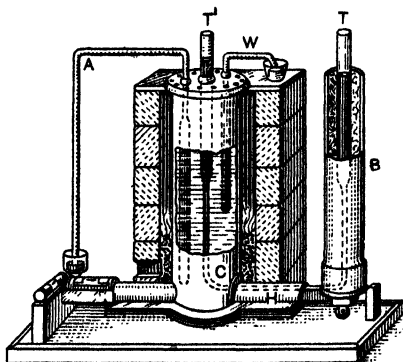


FIG. 50.

round it. The temperature of this oil bath was given by two thermometers—a mercury weight thermometer W, and an air thermometer A (see Chapter VI.). It is interesting to note that this was the first time air was used as a thermometric substance to the exclusion of mercury. It was observed that, at high temperatures, the indications of the two instruments did not agree, and it was decided to base the calculations on the indications of the air thermometer. Indeed, if a mercury thermometer only had been used, the irregularity in the expansion of mercury would not have been detected.

The heights of the columns of mercury were read by means of the cathetometer (see *Properties of Matter*, Wagstaff), which was devised expressly for this purpose. The level of the mercury in T' was first read, then the level in T, and finally the level of the axis of the horizontal tube, H. The difference between the first two readings on the cathetometer scale gave  $(h_t - h_0)$ , and the last two readings gave  $h_0$ . The temperature,  $t^\circ \text{C.}$ , of the oil bath, and therefore of the mercury in the tube T, was given by the air thermometer, A. Thus the mean coefficient of real expansion of mercury could be determined by calculation from these data.

The values of the mean coefficient of real expansion of mercury thus obtained were—

Between $0^\circ \text{C.}$ and $100^\circ \text{C.}$	0.0001818
„ $0^\circ \text{C.}$ „ $200^\circ \text{C.}$	0.0001843
„ $0^\circ \text{C.}$ „ $300^\circ \text{C.}$	0.0001887.

These values show that the expansion of mercury is greater at higher temperatures.

An error in this method is due to the flow of heat from the hot to the cold tube, and thus the mercury in the lower part of the cold column may be heated to an unknown extent. Secondly, in order to make the top of the mercury column visible above the heating apparatus, a little cold mercury was added, thereby introducing an uncertainty as to the average temperature of the hot column. Lastly, owing to the curvature of the surface the mercury columns\* are subjected to a capillary pressure which decreases as the temperature of the surface increases. The difference in the heights of the two columns is affected by this.

A greatly improved form of apparatus (Fig. 51) was devised by **Regnault** to overcome the difficulties mentioned above. The first improvement was to connect the two vertical tubes AC, FN near

their upper ends by a horizontal tube, BG, in the top of which was made a fine pin-hole, O. Hence, when the two tubes were filled with mercury, the height to which the mercury rose was limited by the fact that the superfluous liquid would escape from the pin-hole, and since the globule formed there would be very strongly curved the mercury in the two tubes would stand at a slightly higher level than the pin-hole. Also, when the two tubes, BC, GN, are at different temperatures, the capillary pressure in the colder one, being the greater, forces some mercury across BG and thus increases the length of the projecting column of mercury in the hotter tube until the combined pressure due to capillarity and to the lengths of the columns of mercury is the same in both. Hence, the two columns BC and GN would be subjected to exactly the same pressure at B and G.

Secondly, the horizontal tube connecting the vertical tubes at the bottom was replaced by two bent tubes, CDE, NKL, terminating in a tube, M, which led to an air reservoir. Heat was thus prevented from flowing from the hot to the cold tube. As a further precaution, the horizontal tubes, BO

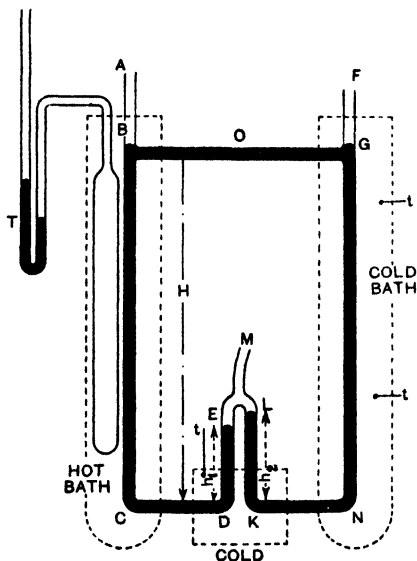


FIG. 51.

and CD, were cooled by means of a stream of cold water.

In carrying out an experiment, mercury was poured into the tubes at A and F, and pressure was applied to M to keep the mercury levels in DE and KL about half-way up the tubes. When the mercury overflowed at O, the tubes were ready for heating.

The dotted lines (Fig. 51) represent the heating and cooling baths, stirrers being provided for each bath. The temperature of the hot bath was measured by an air thermometer, T, and that of the cold bath by mercury thermometers,  $t$ ,  $t'$ . As the heating proceeded, the mercury level in KL rose above that in DE, since hot

mercury is less dense than cold mercury. The vertical distances between the hole, O, and the axes of the tubes, CD, NK, and also the heights of the columns, DE, KL, above the same axes were measured accurately.

Let H be the height of O above the axes of the tubes, CD, KN;  $h_1$  and  $h_2$  the heights of the columns, DE, KL, respectively from the same base line;  $T^\circ \text{C.}$  the temperature of BC, and  $d_T$  the density of mercury at this temperature;  $t^\circ \text{C.}$  the temperature of GN, KL, DE, and  $d_t$  the density of mercury at this temperature. Now, the pressure of the air in M is the same on the tops of the mercury columns in DE, KL. Also, the sum of the atmospheric and capillary pressures is the same at the points level with O in the columns BC, GN. Thus:—

Mercury pressure at E = Mercury pressure at L;

$$\therefore Hd_{1g} - h_1 d_{tg} = Hd_{1g} - h_2 d_{tg},$$

$$\text{or } Hd_r = (H + h_1 - h_2) d_t.$$

If  $c_r$  denote the coefficient of real expansion of mercury, then expressing the above densities in terms of  $d_0$ , the density at  $0^\circ \text{C.}$ ,

$$H \cdot \frac{d_0}{1 + c_r T} = (H + h_1 - h_2) \frac{d_0}{1 + c_r t};$$

$$\therefore 1 + c_r T = \left( \frac{H}{H + h_1 - h_2} \right) (1 + c_r t)$$

$$\text{and } c_r = \frac{h_2 - h_1}{Ht - (H + h_1 - h_2) T}.$$

The great advantage of this method is that the heights to be measured are in vertical lines close together, so that cathetometer errors are minimised. The tubes were of iron, about 150 cm. in length. In all about 130 observations were made with this apparatus, between temperatures of  $0^\circ \text{C.}$  and  $350^\circ \text{C.}$  The results were plotted on a graph, and from the graph the values of the mean coefficient of real expansion of mercury calculated were:—

Between  $0^\circ \text{C.}$  and  $100^\circ \text{C.}$  0.0001815,

„  $0^\circ \text{C.}$  „  $200^\circ \text{C.}$  0.0001841,

„  $0^\circ \text{C.}$  „  $300^\circ \text{C.}$  0.0001866.

These results show that, if the temperature scale is derived from the air thermometer, the coefficient of real expansion of mercury

increases slightly with rise of temperature. In such a case the expansion must be represented by the relation,

$$V_t = V_0 (1 + at + bt^2 + ct^3),$$

instead of the simple relation,  $V_t = V_0 (1 + c_r t)$ .

Regnault's experiment was repeated by Callendar and Moss with improved devices, designed to increase the accuracy of the observations (Fig. 52). The total length of mercury column was increased to about 6 metres, by using six pairs of hot and cold columns connected in series, successive columns being alternately hot and cold. Circulation of the mercury in the tubes was avoided by using narrow tubes. The temperature of the cold columns was maintained by using a mechanically driven paddle to circulate water cooled to  $0^\circ\text{C}$ . by ice through a wide tube completely surrounding the mercury tubes. In the case of the hot columns, an oil bath was used. The oil was heated electrically and a second mechanically driven paddle caused the oil to circulate through a similar tubular bath. The temperatures of the baths were indicated by specially constructed platinum thermometers. The bulbs of these thermometers extended the whole lengths of the baths, so that the mean temperature of each column was determined accurately. The horizontal connecting tubes were cooled by ice-cold water to prevent the conduction of heat from the hot to the cold columns. The heights of the columns of mercury were measured by means of a cathetometer. The difference in height between the hot and cold columns was obtained by using an Invar scale fixed behind the open ends of the tubes, errors due to expansion of the scale thus being minimised.

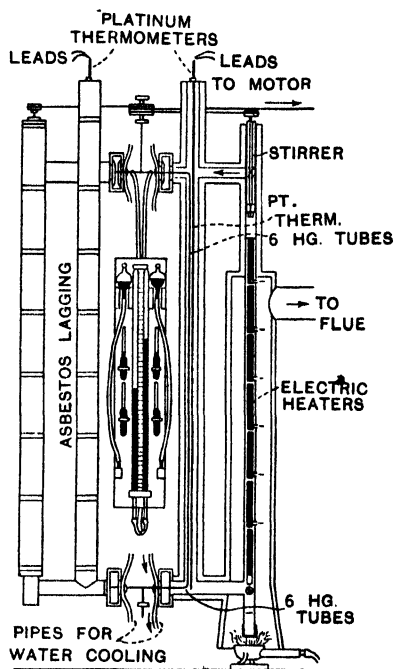


FIG. 52.

The results showed that the mean coefficient of real expansion of mercury between  $0^{\circ}\text{C.}$  and  $t^{\circ}\text{C.}$  is given by the relation

$$c_r = 0.000180555 + 0.071244t + 0.010254t^2,$$

which, for temperatures up to  $200^{\circ}\text{C.}$ , may be reduced to the approximate form

$$c_r = 0.00018016 + 0.072t.$$

Hence the mean coefficient of expansion between  $0^{\circ}\text{C.}$  and  $100^{\circ}\text{C.}$  is  $0.00018205$ . This is also the actual coefficient at  $50^{\circ}\text{C.}$

These results show that the increase in the coefficient of real expansion of mercury with temperature is very small at ordinary temperatures, and therefore the use of the mercury thermometer in all ordinary work is justified.

*Experiment. To find the coefficient of real expansion of a liquid.*—A modified form of Regnault's apparatus (Fig. 53) has been designed for use in the laboratory. This consists of a long piece of glass tubing, BCDEFG, about  $\frac{1}{4}$  inch in diameter bent into the shape of a rectangle as shown, the open ends of the tube being brought close together at B and G, and a small millimetre scale is fixed behind these short lengths. The long vertical portions, CD, EF, of the tube are surrounded as completely as possible by wide glass tubes,  $T_1$  and  $T_2$ , and these wide tubes are also fitted with inlet and outlet tubes so that steam or cold water may be passed through them, as shown. The whole is mounted on a suitable stand.

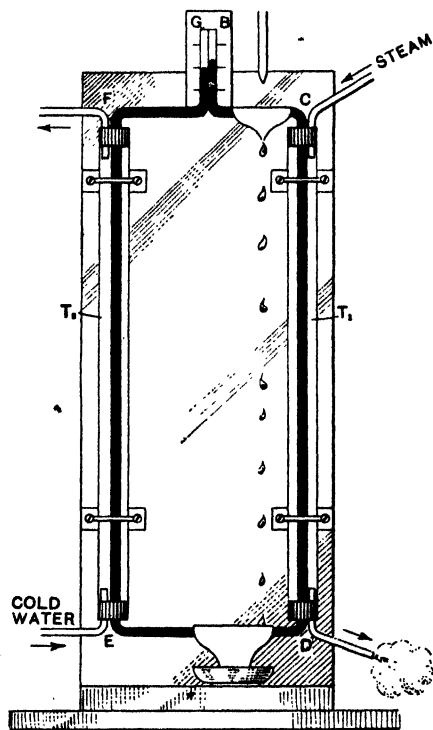


FIG. 53.

together at B and G, and a small millimetre scale is fixed behind these short lengths. The long vertical portions, CD, EF, of the tube are surrounded as completely as possible by wide glass tubes,  $T_1$  and  $T_2$ , and these wide tubes are also fitted with inlet and outlet tubes so that steam or cold water may be passed through them, as shown. The whole is mounted on a suitable stand. Clean dry mercury is poured gradually into the narrow tube, care

being taken to prevent air bubbles remaining in the column. Sufficient mercury is used to fill the tube to a convenient mark on the millimetre scale. The mercury surfaces should give equal readings on the scale.

Steam is passed through the right-hand jacket,  $T_1$ , and a stream of water through the left-hand jacket,  $T_2$ . The temperature of the water on entering and leaving  $T_2$  must be observed. Cold water is allowed to drip on the horizontal tubes near C and D to prevent heat being conducted from the hot column. The mercury gradually acquires the surrounding temperatures, and stands at a higher level in B than in G. The difference in level is observed on the millimetre scale. Also, the difference in level of the horizontal tubes, DE, FC, is measured. Care must be taken to see that the mercury has finished expanding before the readings are taken.

Let  $h_1$  and  $h_2$  be the total heights of the cold and hot columns,  $t_1$  and  $t_2$  the corresponding temperatures. Then, if  $d_1$  and  $d_2$  are the densities of mercury at these temperatures, by equating pressures

$$h_1 d_1 = h_2 d_2.$$

And, if  $d_0$  is the density of mercury at  $0^\circ \text{C.}$ ,

$$h_1 \cdot \frac{d_0}{1 + c_r t_1} = h_2 \cdot \frac{d_0}{1 + c_r t_2};$$

$$\therefore h_1 + h_1 c_r t_2 = h_2 + h_2 c_r t_1,$$

$$\text{and } c_r = \frac{h_2 - h_1}{h_1 t_2 - h_2 t_1}.$$

It will be noticed that  $(h_2 - h_1)$  is equal to the difference of level of the two mercury surfaces at B and G at the end of the experiment. More accurate results will be obtained by this method in the case of liquids such as petroleum and turpentine, which have larger coefficients of expansion.

**Examples.**—(1) Find the coefficient of real expansion of mercury on the Fahrenheit scale.

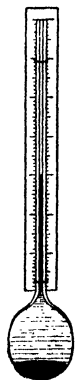
The range of temperature of  $1^\circ \text{F.}$  is only  $\frac{5}{9}$  of the range of  $1^\circ \text{C.}$ ;  $\therefore$  the coefficient of expansion on the Fahrenheit scale is evidently:

$$\frac{5}{9} \times 0.000181 = 0.000101.$$

It was proposed at one time to define the Fahrenheit degree to be such that the coefficient of real expansion of mercury on the Fahrenheit scale was exactly 0.0001.



(2) An alcohol thermometer is to be made from thermometer tubing of 1 mm. bore. 10 degrees of the temperature scale must occupy a length of about 2.5 cm. The bulb must be spherical. Find its internal radius.



Let  $r$  be the radius of the bulb: Volume of bulb =  $\frac{4}{3}\pi r^3$ .

The expansion of alcohol for 10 degrees is approximately  $\frac{4}{3}\pi r^3 \times 10 \times (0.00108 - 0.00003)$  c.c., and this must be equal to  $\pi \times (0.05)^2 \times 2.5$  c.c.

$$\therefore \frac{4}{3} \times r^3 \times 0.0105 = 0.00625;$$

$$\therefore r = \sqrt[3]{\frac{0.00625}{0.014}} = 0.77 \text{ cm.}$$

(3) Determine the ratio between the height of the mercury in the glass vessels of a mercurial pendulum (page 57) and the length of the steel rod so that the distance between the point of suspension and the centre of mass of the mercury may be constant at all temperatures.

If the temperature rises from  $0^\circ \text{C.}$  to  $t^\circ \text{C.}$  the volume of the mercury increases in the ratio  $(1 + 0.000181t) : 1$ , while the area of cross-section of the tube increases in the ratio  $(1 + 0.000009t)^2 : 1$ . The height of the mercury in the vessel increases therefore in the ratio

$$\text{FIG. 54.} \quad \frac{(1 + 0.000181t)}{(1 + 0.00009t)^2} : 1, \text{ or } 1.000163t : 1.$$

If  $h$  is the height of mercury in the vessel at  $0^\circ \text{C.}$ , then  $\frac{h}{2}$  is the distance of its centre of mass from the bottom and  $\frac{h}{2} \times 1.000163t$  is the distance at  $t^\circ \text{C.}$  Hence  $\frac{h}{2} \times 0.000163t$  is the rise of the centre of mass of the mercury relative to the bottom of the tube.

If  $l$  is the length of the steel rod at  $0^\circ \text{C.}$ ,  $l \times 0.000012t$  is the increase of length for  $t^\circ \text{C.}$  Therefore for exact compensation:

$$\begin{aligned} l \times 0.000012t &= \frac{h}{2} \times 0.000163t; \\ \therefore \frac{h}{l} &= \frac{0.000012 \times 2}{0.000163} = 0.15 \text{ approximately.} \end{aligned}$$

## 5. Expansion of Water

The expansion of water has been the subject of numerous experiments. It is of special interest, not only because water is used so generally in physical operations, but also because it presents noteworthy peculiarities. Amongst others, *Pierre, Despretz, Hällstrom,* and *Matthiessen* have studied this matter; the first two used the ordinary dilatometer method, the two latter the hydrostatic method. It is most easily studied, however, by using a constant volume dilatometer.

*Experiment.* Study the expansion of water, using a constant volume dilatometer.—Make a volume dilatometer. Weigh the

dilatometer, fill it with mercury and weigh again. Then pour out six-sevenths of the mercury, thus obtaining a constant volume dilatometer (Art. 3). Find also the area of cross-section of the stem (page 65). Finally fill with water to a convenient mark on the stem. Attach a millimetre scale to the stem (Fig. 54).

Place the bulb in a large bath of ice and water, provided with an accurate thermometer and a stirrer. Take the reading of the liquid column on the scale when it is steady. Warm the water in the bath gently to  $2^{\circ}\text{C}$ . and keep it there for 10 minutes, stirring well. Again take the reading on the scale. Repeat for every  $2^{\circ}$  up to  $10^{\circ}\text{C}$ ., and then for every  $5^{\circ}$  up to  $40^{\circ}\text{C}$ . or above. Check the readings by letting the water cool again to  $0^{\circ}\text{C}$ ., adding ice to the bath to facilitate this. Take the mean of the two readings at any one temperature. Plot a graph, showing how the scale reading varies with temperature. A curve like Fig. 55 will be obtained.

Note that as the heating proceeds the liquid column in the stem falls slowly and then very slowly until a temperature of  $4^{\circ}\text{C}$ . is reached. After this it rises, at first very slowly, and afterwards more rapidly, so long as the temperature is raised. The volume is least therefore at  $4^{\circ}\text{C}$ ., *i.e.* water is at its greatest density at  $4^{\circ}\text{C}$ .

From the smooth curve and the known dimensions of bulb and stem, calculate the coefficient of *real* expansion of water between various temperatures. Taking the volume of 1 gram. of water at  $4^{\circ}\text{C}$ . as 1.0000 c.c., find the volume at other temperatures. (See Table IV., page 395.)

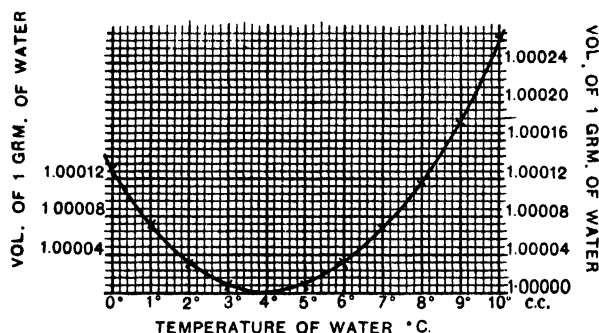


FIG. 55.

With the volume dilatometer water can be cooled much below  $0^{\circ}\text{C}$ . before freezing sets in, and it has been found that expansion takes place continually on cooling, until freezing does set in. A

temperature of  $-20^{\circ}\text{C}$ . has been reached with liquid water. However, at this temperature the slightest jar starts solidification, and the temperature rises to  $0^{\circ}\text{C}$ .

*Hope's Experiment.* Hope devised a simple experiment to determine approximately the temperature of maximum density of water. A tall glass jar, having two side openings fitted with thermometers (Fig. 56), is surrounded at its centre with an outer vessel containing a freezing mixture (page 145). The vessel is filled with water at room temperature, and allowed to cool under the influence of the freezing mixture. As cooling goes on the temperature indicated by the lower thermometer falls steadily, while the upper one shows little change. As the temperature of the lower thermometer, however, approaches  $4^{\circ}\text{C}$ . it falls more and more slowly, and finally becomes stationary; meanwhile, the upper thermometer begins to fall more rapidly, and continues to do so until  $0^{\circ}\text{C}$ . is reached. Ultimately ice may form on the surface of the water, and the lower thermometer remains stationary at  $4^{\circ}\text{C}$ .

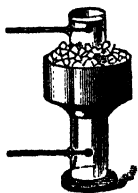


FIG. 56.

The explanation of *Hope's experiment* is simple. The freezing mixture cools the water nearest it. This contracts, becomes denser, and descends, causing the lower thermometer to fall rapidly. This continues so long as a fall of temperature causes the water to contract, but below  $4^{\circ}\text{C}$ . expansion begins, and then the water cooled by the freezing mixture ascends, causing the rapid fall of the upper thermometer to  $0^{\circ}\text{C}$ ., while the lower thermometer remains stationary at the temperature of the lowest, and therefore densest, layer. Its reading consequently indicates approximately the temperature of maximum density of water.

Hope's experiment is merely qualitative, and does not give an accurate determination of the temperature of maximum density of water. The apparatus has, however, been modified slightly by *Despretz* and made to yield accurate results. Four thermometers at different levels were used, and the temperature of each was observed at regular intervals of time. A graph was drawn for each thermometer, showing its fall of temperature with time, and from the curves was deduced, with some accuracy, the temperature of maximum density. The mean value obtained was  $3.98^{\circ}\text{C}$ .

*Joule's Experiment.* Joule adopted a method the principle of which is closely connected with that of Hope's experiment. A

vessel, consisting of two vertical tubes  $4\frac{1}{2}$  ft. high and of diameter 6 in., connected below by a tube fitted with a stop-cock and communicating above by an open channel, was employed (Fig. 57). The vessel was filled with water, so that there was free communication between the two tubes by the upper channel and by the lower tube when the stop-cock was open.

To understand the method of experiment adopted with this apparatus, it must be remembered that, above and below the temperature of maximum density, two temperatures can be found at which the density of water is the same. Thus, the density of water at  $2^{\circ}\text{C}$ . is nearly equal to its density at  $6^{\circ}\text{C}$ . Joule determined, therefore, with this apparatus a series of pairs of temperatures at which water had the same density.

This was done by closing the stop-cock and floating a light glass bead in the upper channel. The temperature of the water in each tube was then adjusted and the stop-cock opened. If the water in one tube was denser than that in the other it sank, and a current was set up, through the lower tube *from* the denser column and through the upper channel *towards* the denser column. The latter current carried the glass bead along with it, and the motion of the bead at once indicated which tube contained the water of higher density. In this way the temperatures were adjusted until the glass bead remained stationary on opening the stop-cock; the mean of the temperatures of the water in each tube then gave the temperature of maximum density. By gradually diminishing the difference of temperature of the water in the two tubes, the temperature of maximum density was found to be  $39.1^{\circ}\text{F}$ ., or  $3.95^{\circ}\text{C}$ .

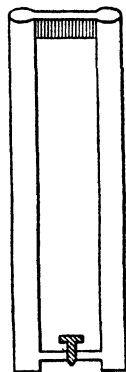


FIG. 57.

It should be noted that Hope's experiment illustrates what actually takes place in pools of water during frosty weather; the surface freezes, but the temperature of the deeper layers of water seldom falls below  $4^{\circ}\text{C}$ . and thus the lives of fish and aquatic animals are preserved. Also, on account of this property, a small pool of water on the surface of a glacier eats its way into the ice, gradually growing deeper.

It should be observed here that water expands on freezing, and thus the ice floats on the surface. If this were not the case, each layer of ice would sink as it was formed, and ultimately all the water in a pool would be converted into ice.

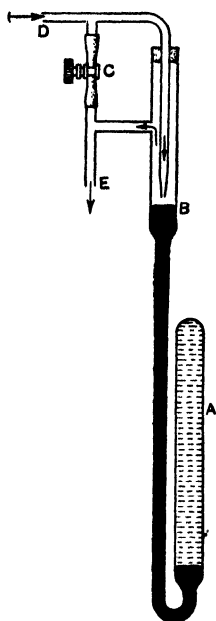


FIG. 58.

## 6. Correction of Barometric Readings for Temperature

The pressure of the atmosphere is usually expressed in terms of the height of a column of mercury at  $0^\circ \text{C.}$  which exerts an equivalent pressure. The *observed* height of a barometer at  $t^\circ \text{C.}$  must be reduced to the *equivalent* height at  $0^\circ \text{C.}$  This is termed correcting for temperature, and in applying the correction two points must be remembered: (1) to correct for the expansion of the scale between  $0^\circ \text{C.}$  and  $t^\circ \text{C.}$ , (2) to correct for the change of density of the mercury.

Let  $H$  denote the *observed* height of the barometer at  $t^\circ \text{C.}$  taken from the scale of the instrument,  $H_0$  the height which would be observed if the whole instrument were at  $0^\circ \text{C.}$ ,  $l$  the mean coefficient of expansion of the material of the scale,  $c_r$  the mean coefficient of real expansion of mercury, and  $t$  the temperature of observation.

The scale readings are correct only at  $0^\circ \text{C.}$  Hence the true height, corrected for the expansion of the scale, is  $H(1 + lt) = H_t$ , say. But  $H_t d_t = H_0 d_0$ , where  $d_t$  and  $d_0$  are the densities of mercury at  $t^\circ \text{C.}$  and  $0^\circ \text{C.}$  Thus:—

$$H(1 + lt) d_t = H_0 d_0,$$

$$\text{or } H_0 = H(1 + lt) \frac{d_t}{d_0}.$$

$$\text{Now (page 67) } \frac{d_t}{d_0} = \frac{1}{1 + c_r t};$$

$$\therefore H_0 = H \frac{(1 + lt)}{(1 + c_r t)} = H[1 + (l - c_r)t].$$

Or, since  $c_r$  is usually greater than  $l$ , this is more generally written

$$H_0 = H[1 - (c_r - l)t].$$

It should be noticed that the mean coefficient of real expansion of mercury is used because the correction (2) is necessary to allow for change of density of the mercury. *On no account must the column of mercury be treated as a rod subject to linear expansion.*

**Example.**—*A barometer with a glass scale reads 755.0 mm. at 18° C.; find the reading at 0° C. The coefficient of real expansion of mercury is 0.000182, and the mean coefficient of linear expansion of glass is 0.000089.*

Applying the above relation:—

$$\begin{aligned} H_0 &= 755 [1 - (0.000182 - 0.000089) 18] \\ &= 755 (1 - 0.000173 \times 18) \\ &= 755 (1 - 0.0031) = 755 - 2.348 \\ &= 752.7 \text{ mm. approximately.} \end{aligned}$$

## 7. Practical Application of Expansion

The expansion of a liquid due to heat may be turned to good account. An example of this is the liquid thermostat. One form of such apparatus is the gas regulator (Fig. 58), which is used to maintain a water-bath at any desired constant temperature. The gas regulator is placed in the bath and the gas passes through it to the burners used to heat the bath, travelling as indicated by the arrows from D to E and thence to the burners. The bulb, A, contains toluene or other similar liquid with a large coefficient of expansion, the lower part of A and the narrow tube containing mercury. When the temperature of the bath increases, the toluene expands, causing the mercury to close the jet at B and cut off the gas supply. The screw, C, is arranged to allow sufficient gas to pass through E to the burners, to avoid complete extinction. When the bath cools, the toluene contracts and the gas supply is restored. The adjustment of the temperature to be maintained in the bath is effected by altering the position of the jet at B.

## CHAPTER VI

### EXPANSION OF GASES

THAT gases expand when heated was shown in Chapter I. by a simple form of apparatus (Fig. 4). Other simple pieces of apparatus (Fig. 59) may be used to illustrate the same fact. The construction needs no description; the liquid used may be mercury, alcohol coloured with magenta dye, or coloured sulphuric acid. To get the column of liquid in the tube warm the reservoir, A, so as to expel some of the contained air, and on cooling dip the open end of the tube in the liquid. If the cork in B fits tightly, a fine hole should be bored through it to enable the air within B to communicate freely with the atmosphere. Any increase or decrease in the temperature of A causes the liquid in the tube to fall or rise, showing expansion or contraction of the volume of the air in A.

*Experiment.* Take a long tube closed at one end, fill it about three-quarters full with mercury, and measure the length of the air column still left in the tube. This air is at the pressure of the atmosphere. Now firmly close the tube with the thumb and invert it in a dish of mercury. Again measure the length of the air column in the tube. It is greater than before, *i.e.* the volume has increased. The pressure of the air in the tube is equal to the barometric height, *less* the height of the mercury column in the tube above the mercury in the dish. Read these two heights and find the difference. It can now be shown that: Barometric height  $\times$  First length of air column = Difference between barometric height and height of mercury column  $\times$  Second length of air column.

*i.e. Pressure  $\times$  volume is a constant.*

This is really an anticipatory proof of Boyle's law (Art. 2): but the point to note here is that the experiment shows that *the volume of a given mass of gas depends upon its pressure as well as upon its temperature.* Hence, in considering the expansion of gases by heat the effect of pressure must not be neglected.

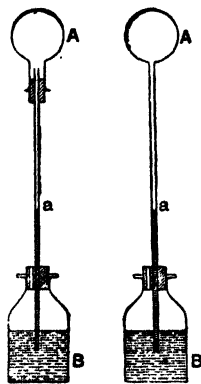


FIG. 59.

### 1. The Relation Between the Volume, Temperature, and Pressure of a Gas

If experiments are to be carried out to find the relation between the volume, temperature, and pressure of a given mass of gas, it is obviously best to divide the experiments into three classes, and thus to find—

(1) The relation between pressure and volume when the temperature is kept constant (Boyle's Law).

(2) The relation between volume and temperature when the pressure is kept constant. This is the simple case of expansion as already studied in the case of solids and liquids (Charles's Law).

(3) The relation between pressure and temperature when the volume is kept constant (Law of Pressures).

From the results of these experiments the relation between volume, temperature, and pressure when all the three are varying can be obtained (Gas Equation).

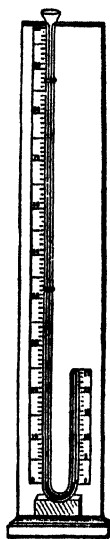


FIG. 60.

### 2. Relation Between Pressure and Volume at Constant Temperature

Boyle stated in 1662 that the volume of a given mass of gas is inversely proportional to the pressure when the temperature is kept constant. This may also be stated as follows:—The product of the pressure and the volume of a given mass of gas at constant temperature is constant,

$$\text{i.e. } P_1V_1 = P_2V_2 = \dots = \text{a constant,}$$

$$\text{or } PV = \text{a constant} \dots\dots\dots (1)$$

Thus if the pressure is doubled, the volume is halved; again, if the volume is to be increased threefold, the pressure must be diminished to one-third of its former value. The law is known as Boyle's Law.

*Experiment .To verify Boyle's law experimentally in the case of air for pressures greater than that of the atmosphere.*—A piece of apparatus known as Boyle's tube (Fig. 60) is generally used. It consists of a piece of stout glass tube of about  $\frac{1}{4}$  in. bore, sealed at one end and bent twice at right angles as shown. A millimetre scale is attached to each limb, having the zeros at the same level



and as low as possible. A small funnel is inserted into the open end for the purpose of pouring in mercury. The experiment should be carried out where the temperature will remain constant and a thermometer near the short limb should be used as a check.

Pour a little mercury into the bend and adjust by shaking until the mercury surfaces are both at the zero of the scales. A mass of air at atmospheric pressure has now been imprisoned in the short limb. Assuming the bore of the tube to be uniform, and taking the volume of unit length of tube as unit volume, the length of the tube may be regarded as the number expressing the volume of air in the closed limb. Read the volume. Pour a little more mercury into the long limb. Note that the mercury does not rise in the closed limb as rapidly as in the open limb: this is due to the pressure exerted by the enclosed air. Read the two mercury levels. Pour in more mercury and repeat the readings. Proceed until the open limb is nearly full.

Now read the barometer to observe the pressure of the atmosphere. The difference in level of the two mercury surfaces in Boyle's tube added to the barometric height is the total pressure exerted on the air, and therefore exerted by the air in the tube. The volume of the air is found by subtracting the reading of the mercury surface in the closed limb from the reading of the top of the tube, since this volume is proportional to the length of the column of air.

Tabulate the readings obtained, find the total pressure and the volume of the air at each observation. Calculate the product of total pressure and volume. The products will be approximately constant. Thus, Boyle's law is verified.

To verify Boyle's law for any other gas, it is necessary only to substitute that gas for air in the closed limb.

**Example.**—10 cub. ft. of oxygen at atmospheric pressure (15 lb. wt. per sq. in.) are compressed in a steel cylinder of 0.6 cub. ft. capacity. Find the pressure of the gas.

$$\text{Applying } P_1 V_1 = P_2 V_2,$$

$$15 \times 10 = P_2 \times 0.6;$$

$$\therefore P_2 = 250 \text{ lb. wt. per sq. in.}$$

A more satisfactory form of apparatus, which may be used for any gas and at pressures above and below that of the atmosphere, is obtainable. A 50 c.c. burette, B, graduated in  $\frac{1}{10}$  c.c. is mounted vertically (Fig. 61) on a stand, which also carries a manometer, M. This consists of a reservoir, R, containing mercury, which can be raised or lowered at will. The reservoir is connected

by a long piece of thick india-rubber tubing to a glass T-piece leading to the lower end of the burette and to a long piece of narrow glass tubing mounted on a vertical scale and open to the atmosphere at its upper end. The upper end of the burette is connected to a glass tube, D, containing calcium chloride, which is also fixed to the stand. The volume of the burette between the uppermost graduation mark and the tap must be obtained.

Clean dry mercury is poured into the reservoir. The tap of the burette is opened and the reservoir is raised gradually until the mercury fills completely the burette. The reservoir is lowered slowly until a suitable volume of air is contained in the burette, the operation being repeated several times so that the air may be dried by the calcium chloride. The tap of the burette is then closed firmly. The volume of air in the burette should be such that the pressure may be reduced below that of the atmosphere by lowering the reservoir.

The barometer is read to observe the pressure of the atmosphere from time to time during the experiment, as it may vary. The temperature of the atmosphere should also be observed from time to time.

The reservoir is moved to different heights on the stand and simultaneous readings of the position of the mercury in the burette and in the reservoir are taken. The position of the mercury in the reservoir is obtained by using the manometer tube on the scale, since both reservoir and tube are open to the atmosphere.

The volume of the air at each stage is obtained directly from the burette readings.

To determine the total pressure on the air in the burette, the barometric pressure at the time must be added to the pressure due to the difference of levels between the mercury in the reservoir and in the burette. This difference of levels is found at the end of the experiment. The reservoir is lowered to the bottom of the stand and the tap of the burette is removed. The reservoir is then raised carefully until the mercury stands in the burette at one of the readings obtained during the experiment. The level of the mercury in the manometer tube is observed. The required

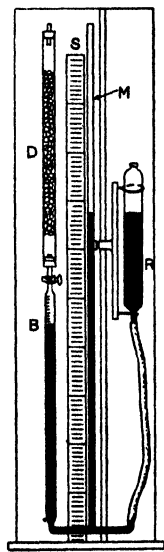


FIG. 61.

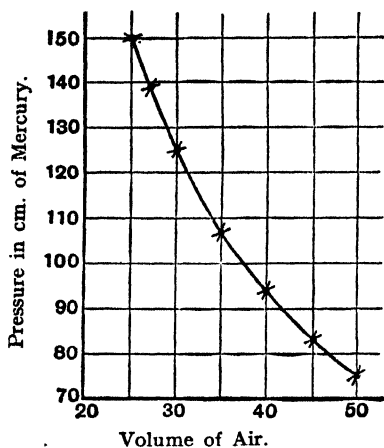


FIG. 62.

a short time should be allowed after each change of pressure for the air to reach the temperature of its surroundings before a reading is taken.

The results obtained by using the apparatus described above may be represented graphically. A curve is plotted between pressure and volume, pressures being ordinates and volumes abscissae. A typical curve (Fig. 62) represents readings taken with a quantity of dry air which at a pressure of 75 cm. of mercury occupied a volume of 50 c.c. and which was compressed in stages to half the volume.

Accurate results with a gas obeying Boyle's law perfectly are represented by a rectangular hyperbola. It is difficult, however, to use a curve of this type as a test of the accuracy of the results. A better test is afforded

difference of level is the difference between this reading and the corresponding reading obtained when the tap of the burette was closed. This is repeated for each of the burette readings observed.

The various readings should be tabulated as the experiment proceeds, accurate values of the pressure and volume thus being obtained. The changes of pressure should be effected slowly, as a sudden compression or expansion of the air in the burette causes it to be warmed or cooled. Also,

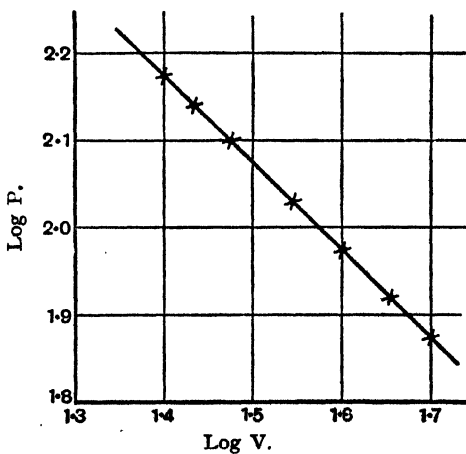


FIG. 63.

by plotting the logarithm of the pressure against the logarithm of the volume.

Since Boyle's law is written  $PV = \text{a constant}$ ,

by taking logarithms,  $\log P + \log V = \text{a constant}$ .

Therefore, by plotting  $\log P$  against  $\log V$ , a straight line is obtained, which is inclined at an angle of  $45^\circ$  to either axis when the quantities are plotted to the same scale (Fig. 63, which is obtained from the same data as Fig. 62).

A curve which represents the relation between the pressure and volume of a body at constant temperature is called an **isothermal curve**. Thus, the isothermal of a gas such as air is a rectangular hyperbola.

### 3. Relation Between Volume and Temperature at Constant Pressure

It has been shown that every solid and liquid has its own coefficient of expansion which is always a very small fraction. However, all gases have nearly the *same* coefficient of expansion, and it is *not* a very small fraction.

*Experiment.* To show that all gases have the same coefficient of expansion.—Take a clean dry litre flask, F (Fig. 64), fill it with dry air, and fit it with a stopper carrying a short delivery tube, D, leading to a trough containing water in which is placed a bee-hive shelf, A. A clamp supports the apparatus at C. Immerse the flask, F, in a large beaker, B, filled with water. Heat the water in the beaker gently, stirring well, up to  $20^\circ \text{C}$ ., noting the temperature by a thermometer, T. When the temperature has reached  $20^\circ \text{C}$ . and bubbles have ceased to escape from the mouth of D, place over it an inverted graduated gas-jar, G, of 200 c.c. capacity, which has been filled with water.

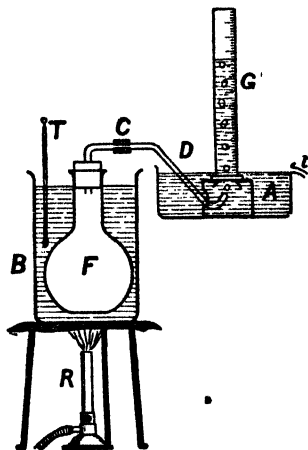


FIG. 64.

Now heat B until the water boils, placing a few fragments of unglazed earthenware in the beaker to prevent the water bumping as it boils. When the bubbles have ceased to rise in G, note the

volume of air collected. The volume of air in G is the volume, measured at the temperature of the water in G, by which the quantity of air which filled F at a temperature of  $20^{\circ}\text{C}$ . is increased when heated to  $100^{\circ}\text{C}$ .

Repeat the experiment after filling F in turn with coal-gas, hydrogen, or other common gases. It will be found that the volume of gas which overflows into the graduated cylinder is the same in each case.

The experiment just described is more or less qualitative. The earliest accurate experiments were made by Dalton in England, by a method somewhat similar in principle to this experiment. About the same time Gay-Lussac, in France, carried out experiments.

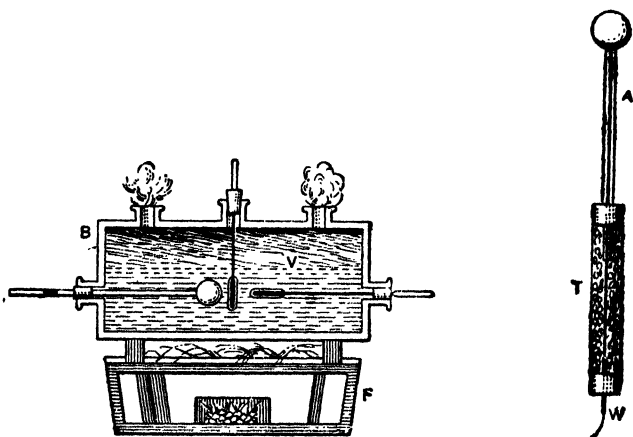


FIG. 65.

(1) GAY-LUSSAC'S METHOD OF FINDING THE COEFFICIENT OF EXPANSION OF A GAS AT CONSTANT PRESSURE.—For the purpose of this determination, Gay-Lussac obtained a wide thermometer tube with a spherical reservoir and a long stem. This tube was carefully calibrated and graduated. It was then filled with mercury and fitted into a wider tube, T (Fig. 65), containing calcium chloride. By introducing a platinum wire, W, into the tube the mercury was slowly shaken out, and its place was taken by air which was quite dry owing to it having passed over the calcium chloride in the wide tube. A short column of mercury was left in the stem of the tube to serve as an index. Then the tube was placed horizontally in a sheet-iron vessel, V, which was first filled

with melting ice and afterwards placed on a furnace, F, and gradually heated. The position of the mercury index was noted when the bulb was surrounded with ice, and also at different temperatures as the heating proceeded. The temperatures were observed by a mercury thermometer.

From these observations, the mean coefficient of *apparent* expansion of air in glass was calculated, and the mean coefficient of *absolute* expansion was deduced from this result and the known mean coefficient of expansion of the glass. In this way Gay-Lussac found the mean coefficient of absolute expansion of air at constant pressure (atmospheric) to be 0.00375, or  $\frac{1}{268}$ . This result is now known to be too high.

(2) A LABORATORY METHOD.—*Experiment.* To find the mean coefficient of expansion of air at constant pressure. A piece of tubing, A (Fig. 66), about 2 ft. long and of  $\frac{1}{8}$  in. bore is carefully cleaned and dried, and sealed at one end. The bore must be uniform. The tube is heated and the open end dipped in strong sulphuric acid. As the tube cools, acid will be drawn up into it. In this

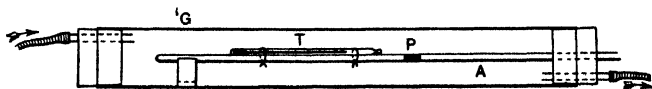


FIG. 66.

way a thread of acid, P, about an inch in length is introduced. This will serve as an index, and also to dry effectually the enclosed air. When the tube is cold, the thread should be about half-way along the tube. Fasten a thermometer, T, to the tube, and mount the tube by corks in a wide glass tube, G, so that the open end just projects. Then fix the outer tube horizontally, and provide it with corks, so that a current of water or steam may be passed through it.

Pass a stream of ice-cold ( $0^{\circ}\text{C}.$ ) water through G. When the thread becomes stationary, measure as accurately as possible the distance between the closed end of the tube and the innermost end of the thread. This length is proportional to the volume of the air at  $0^{\circ}\text{C}.$  Now pass a steady current of steam through G. The air in A will expand and force the thread outwards. The expansion will be at atmospheric pressure because the outermost end of the thread is exposed to the atmosphere. When the thread becomes stationary, measure again the distance of the thread from the closed end. This length is proportional to the volume of the air at  $100^{\circ}\text{C}.$

If the volume at  $0^{\circ}\text{C.}$  is denoted by  $V_0$ , and that at  $100^{\circ}\text{C.}$  by  $V_{100}$ , then the mean coefficient of apparent expansion of air in glass at constant pressure between  $0^{\circ}\text{C.}$  and  $100^{\circ}\text{C.}$  is given by—

$$c_a = \frac{V_{100} - V_0}{100V_0},$$

and the mean coefficient of real expansion of air between these temperatures is given by

$$c_r = c_a + c,$$

where  $c$  is the coefficient of expansion of glass. Since  $c_a$  is much greater than  $c$ , and the above experiment is only rough, it is not worth while correcting for the expansion of glass.

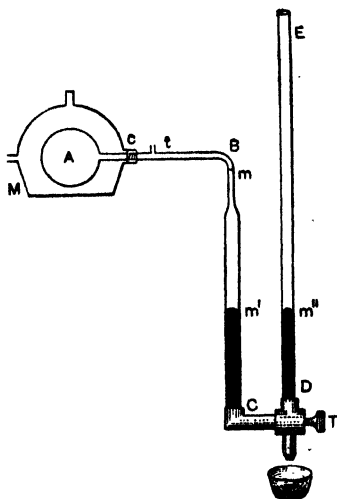


FIG. 67.

(3) REGNAULT'S METHOD OF FINDING THE COEFFICIENT OF EXPANSION OF A GAS AT CONSTANT PRESSURE.—There are two important sources of error in Gay-Lussac's method; (a) the moisture clinging to the inner surface of the thermometer tube was not removed and, being converted into vapour on heating, the volume of the enclosed air appeared to increase more than it really did, the result obtained being too high in consequence; (b) the mercury index in the stem did not completely seal

the enclosed air from the outer air. A method was devised by Regnault to avoid these errors. The interior of the vessel which contained the gas was dried thoroughly by alternately exhausting it by means of an air pump and filling it with dry warm gas. The mercury index was replaced by a long column of mercury in a U-tube manometer.

The reservoir, A (Fig. 67), in which the gas was placed, was a small spherical vessel enclosed in a metal vessel, M, and the temperature of the gas contained was adjusted by filling the space between the two vessels with ice, water, steam, etc. The manometer, BCDE, consisted of two vertical tubes communicating at

the bottom by a metal bend to which a tap, T, was fitted, and the whole was immersed in a water-bath in order to keep it at a uniform known temperature. The tube, BC, ended in a narrow piece of tubing, bent at B and joined to the stem of A. The other tube, DE, was much longer. Between B and A was fitted a small side tube, *t*, by means of which the interior of A was dried, and the gas introduced into it after passing through a series of drying-tubes.

To perform an experiment, the vessel, A, was surrounded with melting ice and mercury poured into the manometer at E until it reached the mark, *m*, on the tube, BC, and to a point in DE on the same horizontal line as *m*. This adjustment of levels was effected by varying the quantity of gas in A through *t*. The tube, *t*, was then sealed in a blow-pipe flame, the ice in M removed, and a small quantity of water put in its place and heated until it boiled. The vessel, A, was thus surrounded with steam at the temperature of the boiling point, the gas expanded and, depressing the mercury column in BC, caused that in DE to rise. The tap, T, was then opened and some mercury run out. As the gas expanded further, more and more mercury was run out until, when the expansion was complete, the levels of the mercury columns in BC and DE were adjusted in the positions *m'* and *m''* in the same horizontal line.

Thus the gas in A expanded, between  $0^{\circ}\text{C.}$  and  $t^{\circ}\text{C.}$ , at a constant pressure equal to that of the atmosphere at the time of the experiment, for at both temperatures the mercury columns in the manometer were adjusted so as to have no difference of level. If, then, the volume of A, the volume of the stem up to *m*, and the volume of BC between *m* and *m'* were known, the mean coefficient of absolute expansion could be calculated in the usual way.

It should be noted that the gas in the part of the apparatus outside M was at a different temperature from that in A, hence a correction for this as well as for the expansion of the glass was applied. These corrections were small since the volume of gas in A is large compared with that in BC, and the coefficient of expansion of glass is less than  $\frac{1}{100}$  that of the gas.

Regnault found by this method the value 0.0036706 for the mean coefficient of absolute expansion of air at atmospheric pressure between the freezing and boiling points of water. For different gases the value of this coefficient varied slightly, especially in the case of gases which are liquefied easily. This result, however, which is approximately equal to  $\frac{1}{273}$ , may be considered as applicable to most gases.



(4) OTHER LABORATORY METHODS.—*Experiment (a).* To show that the expansion of air is uniform and to determine the coefficient at constant pressure.—Modify the apparatus of Fig. 66 by bending the tube near the open end and using a long metal water-bath (Fig. 68). Make several marks on the tube at various distances from the closed end. Heat the bath slowly, stir well, and take the temperatures as the inner end of the liquid index reaches the marks. The temperature should be kept constant for a minute or two before taking the reading. Finally measure the distances of the marks from the closed end of the tube. Tabulate these distances and the temperatures. Plot a graph between lengths and temperatures. The graph will be a straight line, showing that the expansion is uniform. Deduce the coefficient of expansion from the graph.

**Example.**—In an experiment with a tube of uniform bore, marks were made at distances of 36, 38, 40, 42, etc., cm. from the closed end of the tube. The experiment was commenced at  $0^{\circ}\text{C.}$ , when the near end of the index was between the first and second marks. The temperatures at which it reached the other marks were  $14^{\circ}\text{C.}$ ,  $29^{\circ}\text{C.}$ ,  $44^{\circ}\text{C.}$ ,  $58^{\circ}\text{C.}$ ,  $74^{\circ}\text{C.}$ ,  $88^{\circ}\text{C.}$ , and when

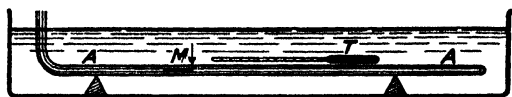


FIG. 68.

the water boiled it did not reach the eighth mark. Plot the graph (Fig. 69). Draw the straight line, AB.

From this line  $V_0$ , given by A, = 36.0 cm., and  $V_{100}$ , given by B, = 49.5 cm. Hence, the coefficient of apparent expansion of air in glass at constant pressure is given by:—

$$c_a = \frac{49.5 - 36.0}{100 \times 36} = \frac{13.5}{3600} = 0.00375.$$

*Experiment (b).* Another method of finding the coefficient of expansion of air at constant pressure.—The principle of the weight thermometer may be applied to determine the coefficient of expansion of a gas at constant pressure, and was also used by Regnault in the case of air. The weight thermometer after being filled with dry air is heated, say to  $100^{\circ}\text{C.}$ , with the open end just dipping under the surface of mercury in a dish. When no more air is expelled the vessel (and mercury) is cooled to  $0^{\circ}\text{C.}$  and mercury flows into the tube, partly filling the bulb. The pressure of the air remaining in the thermometer is then adjusted to that of the atmosphere, the mouth of the stem is closed and the thermometer withdrawn from

the mercury in the dish. It is then weighed. From this weight and the weight of the empty vessel, the weight of mercury now in the tube can be found,  $m$  grm. Finally, the thermometer is completely filled with mercury at  $0^\circ \text{C.}$  and weighed again, so that the weight of the mercury which fills the tube at  $0^\circ \text{C.}$  is found,  $M$  grm.

Then,

$$\frac{\text{Volume of air which fills the thermometer at } 100^\circ \text{C.}}{\text{Volume of the same quantity of air at } 0^\circ \text{C.}} = \frac{M}{M - m};$$

$$\therefore 1 + 100c_a = \frac{M}{M - m} = 1 + \frac{m}{M - m}.$$

$$\text{Hence } c_a = \frac{m}{100(M - m)}.$$

More generally, if the temperatures are  $t_1^\circ \text{C.}$  and  $t_2^\circ \text{C.}$ , instead of  $0^\circ \text{C.}$  and  $100^\circ \text{C.}$ ,

$$\frac{1 + c_a t_2}{1 + c_a t_1} = \frac{M}{M - m}$$

$$\text{and } c_a = \frac{m}{M(t_2 - t_1) - mt_2}.$$

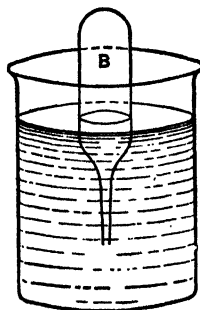


FIG. 70.

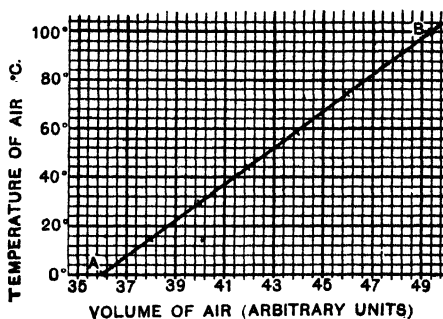


FIG. 69.

The experiment is more easily performed if water is used instead of mercury. The results are not quite so accurate, but the experiment serves to illustrate the principle involved.

Make a bulb B (Fig. 70) from a piece of glass tubing, drawing out the neck to a very narrow stem. Weigh the bulb. Fix the bulb, with stem upwards, in a clamp so that as much of it as possible is immersed in water in a large beaker. Boil the water and take its temperature,  $t_2^\circ \text{C.}$  After about 10 minutes, seal the open end of the stem.

Now take the bulb, invert it in cold water in a large beaker (Fig. 64) and break off the tip of the stem. The water rises in the bulb. Support the bulb in a clamp, adjust its position until the water inside is level with the water outside and leave it for 10 minutes to acquire the temperature of the water. Take this temperature,  $t_1^\circ \text{C}$ . While the bulb is still in position, close the mouth of the stem carefully and remove the bulb. Dry the outside and weigh (including the fragment broken off).

Lastly, fill the bulb completely with water, adjusting the temperature of the water to  $t_1^\circ \text{C}$ . before withdrawing the neck. Dry and weigh again.

*Example.*—In an experiment the weight of the bulb was 7.14 gm. When partly filled with water at  $9^\circ \text{C}$ . it weighed 14.67 gm., and when completely filled with water at  $9^\circ \text{C}$ . it weighed 37.35 gm. The boiling water was at a temperature of  $101^\circ \text{C}$ . Find the coefficient of expansion of air at constant pressure.

$$\frac{\text{Volume of air filling bulb at } 101^\circ \text{C.}}{\text{Volume of same air at } 9^\circ \text{C.}} = \frac{37.35 - 7.14}{37.35 - 14.67} = \frac{30.21}{22.68},$$

$$\text{i.e. } \frac{1 + 101c_a}{1 + 9c_a} = \frac{30.21}{22.68},$$

$$\therefore \frac{92c_a}{1 + 9c_a} = \frac{7.53}{22.68} \quad \text{and} \quad c_a = 0.0037.$$

(5) DALTON'S, GAY-LUSSAC'S, OR CHARLES'S LAW.—The fact that air and other gases expand uniformly when heated at constant pressure was first discovered by Charles and Dalton, and afterwards verified by Gay-Lussac, and more accurately by Regnault. The formular expression of this fact is known as Dalton's, Gay-Lussac's, or Charles's Law, and it may be enunciated: The coefficient of expansion of any gas under constant pressure is  $\frac{1}{273}$ . Or, If the temperature of any given mass of gas, whose pressure is maintained constant, is raised by  $1^\circ \text{C}$ ., the volume increases by  $\frac{1}{273}$  of the volume it would have at  $0^\circ \text{C}$ . under the same pressure.

If the volume at  $0^\circ \text{C}$ . is denoted by  $V_0$ , and the volume of the same mass of gas at  $t^\circ \text{C}$ . by  $V_t$ , then

$$V_t = V_0 (1 + c_r t) \quad \text{and} \quad c_r = \frac{1}{273} \dots \dots \dots (2)$$

Also, if  $V_1$  and  $V_2$  are the volumes of the same mass of gas at  $t_1^\circ \text{C}$ . and  $t_2^\circ \text{C}$ .,

$$\frac{V_1}{V_2} = \frac{1 + c_r t_1}{1 + c_r t_2}.$$

In the case of Regnault's experiments the pressures used were in the neighbourhood of that of the atmosphere, but, of course, by

using greater pressures the coefficient of expansion of the gas in a state of greater density may be determined. It is found that the coefficient increases slightly as the pressure increases. In the case of air, the variation is represented by the relation  $c_r = 0.0036605 + 0.00781\rho$ , where  $\rho$  is the density. In Regnault's experiments  $\rho = 0.001293$  gm. per c.c. and therefore  $c_r = 0.0036706$ .

The coefficient also varies with temperature, very slightly at ordinary and high temperatures, but appreciably at low temperatures, especially when the gas is approaching the temperature of liquefaction.

#### 4. Relation Between Temperature and Pressure at Constant Volume

When a gas is heated in a closed vessel so that it cannot expand, it is obvious from previous knowledge that its pressure must increase.

The relation between pressure and temperature for gases at constant volume was also investigated by Regnault, using the apparatus already described (Art. 3, Fig. 67). The method of using the apparatus was somewhat similar, with the difference that in order to keep the volume of gas constant, the mercury column was always brought back to *m* in BC. This was done by pouring mercury in ED at E. The pressure was then obtained by observing the difference of level of the mercury in BC and EC, and the pressure of the atmosphere.

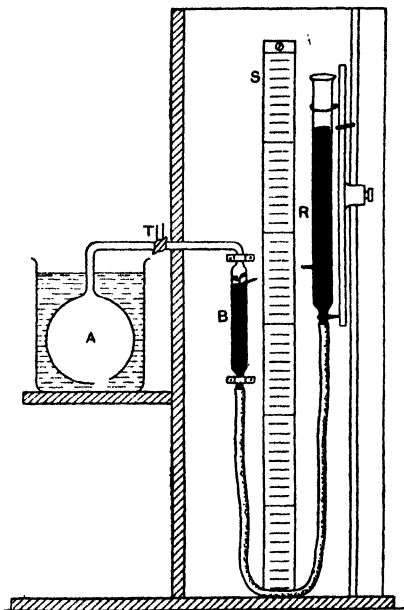


FIG. 71.

*Experiment.* To find the coefficient of increase of pressure with temperature of air at constant volume.—A standard form of apparatus suitable for this experiment is shown (Fig. 71). A bulb, A, about 3 in. in diameter is connected by a glass tube of narrow bore, bent twice at right angles, to a wider tube, B, fixed vertically on a stand

provided with a millimetre scale. The lower end of B is connected by a long piece of thick india-rubber tubing to a reservoir, R, containing mercury, which can be raised or lowered at will. A pointed index, usually of blue glass, is fixed inside B near the top. The three-way tap and side tube, T, enables the bulb to be filled with dry air. A large beaker or copper vessel is supported so that A may be completely immersed in water.

Fill the bath with ice and water. The temperature of A gradually reaches  $0^{\circ}\text{C}$ . Adjust the position of R so that the mercury surface in B reaches the fixed mark, which should be as near the bulb as possible. Read the level of the mercury surface in R, and the height of the barometer. If this is  $H$ , then  $P_0$ , the pressure of the air at  $0^{\circ}\text{C}$ . in A is given by  $H \pm h$  where  $h$  is the difference between the levels of the mercury surfaces in B and R.

Now heat the bath. As the temperature rises the air in A will expand and force the mercury down in B. Prevent this by raising R so that the mercury is brought back to the index. Proceed until the temperature is  $20^{\circ}\text{C}$ ., stirring well, and keep the bath at  $20^{\circ}\text{C}$ . for some time. Finally adjust R until the mercury is exactly at the index, read the height of the mercury in R, and deduce the pressure of the air in A at  $20^{\circ}\text{C}$ . as before. Repeat the observations with the bath at temperatures of  $40^{\circ}\text{C}$ .,  $60^{\circ}\text{C}$ .,  $80^{\circ}\text{C}$ ., and  $100^{\circ}\text{C}$ . Tabulate the results. Plot a graph taking temperatures as abscissae and pressures as ordinates. The graph will be a straight line, showing that the pressure increases uniformly with temperature.

Show also, by calculation, that  $(P_t - P_0)/P_0 \cdot t$  is a constant, where  $P_t$  is the pressure found at each of the temperatures,  $t^{\circ}\text{C}$ ., used. If the experiment is performed carefully, it will be found that this constant is  $\frac{1}{273}$ .

**Example.**—The following table shows a set of observations:—

TEMPERATURE	PRESSURE	INCREASE OF PRESSURE	INCREASE OF PRESSURE PER DEGREE ABOVE $0^{\circ}\text{C}$ .
$0^{\circ}\text{C}$ .	760 mm.	—	—
$21^{\circ}\text{C}$ .	818 mm.	58 mm.	2.79 mm.
$32^{\circ}\text{C}$ .	849 mm.	89 mm.	2.78 mm.
$54^{\circ}\text{C}$ .	910 mm.	150 mm.	2.78 mm.
$75^{\circ}\text{C}$ .	968 mm.	208 mm.	2.77 mm.
$100^{\circ}\text{C}$ .	1038 mm.	278 mm.	2.78 mm.

The mean value from column (4) = 2.78;

$$\therefore \text{Coefficient of increase of pressure} = \frac{2.78}{760} = \frac{1}{274}.$$

The results of the above experiment show that—

$$P_t = P_0 (1 + c_{ap}t)$$

where  $c_{ap}$  is the coefficient of increase of pressure at constant volume *uncorrected for the expansion of the vessel*, and  $t$  is the temperature Centigrade. Also,  $c_{ap} = \frac{1}{273}$  approximately.

The correction for the expansion of the bulb may be applied in the usual manner. Thus, if  $c_p$  is the coefficient of real increase of pressure at constant volume, and  $c$  is the coefficient of expansion of the vessel,

$$c_p = c_{ap} + c.$$

The value of  $c$  is so small that usually it is smaller than the probable error in  $c_{ap}$ , hence the correction is negligible.

The increase in pressure of air and other gases, when heated at constant volume; was first established by Regnault. The formulæ expression of this fact, known as the law of pressures, may be enunciated:—If the temperature of any given mass of gas, whose volume is kept constant, is raised by  $1^\circ \text{C.}$ , the pressure is increased by  $\frac{1}{273}$  of the pressure at  $0^\circ \text{C.}$

If the pressure at  $0^\circ \text{C.}$  is denoted by  $P_0$  and the pressure of the same mass of gas at  $t^\circ \text{C.}$  by  $P_t$ , then—

$$P_t = P_0 (1 + c_p t) \quad \text{and} \quad c_p = \frac{1}{273} \dots \dots \dots (3)$$

Also, if  $P_1$  and  $P_2$  are the pressures of the same mass of gas at  $t_1^\circ \text{C.}$  and  $t_2^\circ \text{C.}$ ,

$$\frac{P_1}{P_2} = \frac{1 + c_p t_1}{1 + c_p t_2}$$

As a result of his experiments on air Regnault found that  $c_p = 0.0036650$ , which is slightly less than  $c_r$ . Similar results were obtained for other gases.

In general, the two coefficients,  $c_r$  and  $c_p$ , are so nearly equal that for all practical purposes they are taken as identical and equal to  $\frac{1}{273}$  (0.003663). In the work which follows,  $c$  or  $\frac{1}{273}$  will be used indiscriminately for  $c_r$  and  $c_p$ .

## 5. Absolute Temperature

Consider an apparatus similar to that used above (Fig. 68) for the investigation of the increase of volume of air at constant pressure. Suppose that the tube is a very long one of uniform bore, and suppose that the air in the tube when at  $0^\circ \text{C.}$  occupies 273 cm. of the length of the tube. If this tube were plunged into

steam from water boiling at the normal atmospheric pressure, the air would expand showing an increase of volume equal to  $\frac{1}{273}$  of its volume at  $0^{\circ}\text{C}$ . Hence, at  $100^{\circ}\text{C}$ . the air would occupy 373 cm. of the length of the tube, and if the space of 100 cm. between the freezing point and the boiling point is divided into 100 equal parts of 1 cm., each division corresponds to  $1^{\circ}\text{C}$ . In other words, the tube can be considered as a simple thermometer. If now this method of division is continued along the tube below the freezing point, the reading at the closed end of the tube will be  $-273^{\circ}\text{C}$ . This temperature is called the **absolute zero**. If temperatures are reckoned from this point *as zero*, the freezing point is denoted by  $273^{\circ}\text{Absolute}$  (written  $273^{\circ}\text{A.}$ ) since it is  $273^{\circ}\text{C}$ . higher, and the boiling point is at  $373^{\circ}\text{A.}$  Generally,  $t^{\circ}\text{C}$ . becomes  $(273 + t)^{\circ}\text{A.}$ , which is written  $T^{\circ}\text{A.}$

Since this zero is at the closed end of the tube, it would imply that at this temperature the volume of the air is reduced to zero. This result is, of course, impossible physically and can be realised only if it is assumed that air remains a gas throughout the whole range of temperature from  $0^{\circ}\text{C}$ . to  $-273^{\circ}\text{C}$ . This is not the case, for it liquefies at  $-183^{\circ}\text{C}$ ., *i.e.*  $90^{\circ}\text{A.}$ , and solidifies at a lower temperature, so that its law of contraction would change completely at these low temperatures.

Although the supposition on which the above determination of the absolute zero is based is very crude, yet the value thus obtained differs only by a fraction of a degree from the accurate value obtained by Kelvin and by Callendar by very rigid calculation.

In dealing with problems relating to gases, it is exceedingly convenient to measure temperatures from this absolute zero, for then it may be stated that the volume of a given mass of gas at constant pressure is proportional to its absolute temperature. Thus, in the case of the simple air thermometer used above, if the volume of 1 cm. of its length be denoted by  $v$ , then the volume at  $273^{\circ}\text{A.}$  is  $273v$ , at  $373^{\circ}\text{A.}$  it is  $373v$ ., and at  $T^{\circ}\text{A.}$  it is  $Tv$ ;

$$\therefore \frac{V_1}{V_2} = \frac{273 + t_1}{273 + t_2} = \frac{T_1}{T_2} \dots \dots \dots (4)$$

where  $T_1^{\circ}$  and  $T_2^{\circ}$  denote absolute temperatures corresponding to  $t_1^{\circ}\text{C}$ . and  $t_2^{\circ}\text{C}$ . This can also be derived from the relation (page 94)  $V_1/V_2 = (1 + ct_1)/(1 + ct_2)$ . Here  $c = 1/273$ , and therefore:—

$$\frac{V_1}{V_2} = \frac{1 + \frac{1}{273} \cdot t_1}{1 + \frac{1}{273} \cdot t_2} = \frac{273 + t_1}{273 + t_2} = \frac{T_1}{T_2}$$

From this, *Charles's law* may be stated in the simple form:—The volume of a given mass of any gas at constant pressure varies directly as the absolute temperature,

$$\text{i.e. } \frac{V}{T} = \text{a constant, when } P \text{ is constant} \dots\dots\dots (5)$$

**Example.**—A given mass of oxygen occupies 24.0 c.c. at 15° C. Find its volume at 25° C. if the pressure is unchanged.

$$15^{\circ} \text{ C.} = (273 + 15)^{\circ} \text{ A. and } 25^{\circ} \text{ C.} = (273 + 25)^{\circ} \text{ A.}$$

Applying Charles's Law, viz.  $V_1/T_1 = V_2/T_2$ :—

$$\frac{24}{273 + 15} = \frac{V_{25}}{273 + 25}; \quad \therefore V_{25} = 24 \times \frac{298}{288} = 24.8 \text{ c.c.}$$

In the same way, if the law of variation of pressure with temperature is considered, it is found that the pressure exerted by a given mass of gas kept at constant volume is proportional to its absolute temperature. Thus, if the pressure at 0° C. is that due to 273 mm. of mercury, then since the pressure at constant volume increases or decreases by  $\frac{1}{273}$  of its value at 0° C. for a change of temperature of 1° C., the pressure at 100° C. is 373 mm., and at - 273° C. it is 0 mm. If the temperatures are expressed as absolute temperatures, then, the pressure at 373° A. is that due to 373 mm. of mercury, at 273° A. it is that due to 273 mm. of mercury and at 0° A. it is zero. In other words, the pressure is directly proportional to the absolute temperature. This can also be derived from the relation (page 97)

$$\begin{aligned} \frac{P_1}{P_2} &= \frac{1 + \alpha t_1}{1 + \alpha t_2} = \frac{1 + \frac{1}{273} t_1}{1 + \frac{1}{273} t_2} \\ \therefore \frac{P_1}{P_2} &= \frac{273 + t_1}{273 + t_2} = \frac{T_1}{T_2} \dots\dots\dots (6) \end{aligned}$$

Thus, the *law of pressures* may be stated:—The pressure of a given mass of any gas at constant volume varies directly as the absolute temperature,

$$\text{i.e. } \frac{P}{T} = \text{a constant, when } V \text{ is constant} \dots\dots\dots (7)$$

**Example.**—A mass of gas at - 73° C. exerts a pressure of 60 cm. of mercury. Find the pressure it will exert at 27° C. if the volume is unchanged.

$$- 73^{\circ} \text{ C.} = (273 - 73)^{\circ} \text{ A. and } 27^{\circ} \text{ C.} = (273 + 27)^{\circ} \text{ A.}$$

Applying the law of pressures, viz  $P_1/T_1 = P_2/T_2$ :—

$$\frac{60}{273 - 73} = \frac{P_{27}}{273 + 27};$$

$$\therefore P_{27} = 60 \times \frac{300}{200} = 90 \text{ cm. of mercury.}$$



The two relations which have thus been established are of great importance. It must be remembered that the first relation is true only if *pressure* is constant, and the second is true only if *volume* remains constant.

## 6. Graphical Representation of Change of Volume with Temperature

The graph showing how the volume of a given mass of gas varies with the temperature when the pressure is kept constant is approximately a straight line over ordinary ranges of temperature, such as  $V_0V_{100}$  (Fig. 72). This has been proved above (Fig. 69). If this line is extended on the side of lower temperature, it will be found to cut the temperature axis at the temperature  $-273^\circ\text{C}$ . This is the graphic representation of the fact deduced in Art. 5, that the absolute zero of the air thermometer is  $-273^\circ\text{C}$ . As

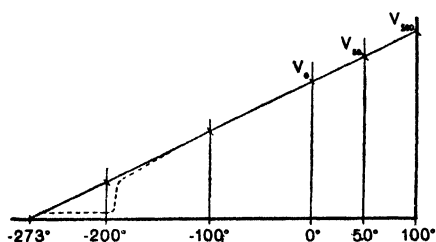


FIG. 72.

explained then, it is a physical impossibility that this graph should represent truly the change of volume as the temperature is reduced to  $-273^\circ\text{C}$ . The graph for these low temperatures represents only what would happen if Charles's law were applicable at all temperatures.

What actually takes place is indicated, *in a general way*, by the dotted line (Fig. 72) drawn for air. At normal pressure air liquefies at  $-183^\circ\text{C}$ . and as the temperature approaches this value, the volume of the air diminishes more rapidly than Charles's law demands. At  $-183^\circ\text{C}$ . the volume decreases suddenly from that occupied by the gas at this temperature to the volume of the corresponding liquid at this temperature. Below  $-183^\circ\text{C}$ . the volume of the liquid decreases very slowly with fall of temperature, but never becomes zero, *i.e.* the dotted line gradually approaches the temperature axis, but does not reach it.

A curve which represents the relation between the volume and temperature at constant pressure is called an *isopiestic*. A curve which represents the relation between pressure and temperature at constant volume is called an *isometric*. (A curve which represents the relation between volume and pressure at constant temperature is called, as already stated, an *isothermal*.)

## 7. General Relation Between Pressure, Volume, and Temperature

If  $P$ ,  $V$ , and  $T$  denote the pressure, volume, and absolute temperature of a given mass of gas, it is possible to establish for these three quantities a general relation which embodies the three laws discussed above.

From Boyle's law,  $V \propto \frac{1}{P}$  when  $T$  is constant.

From Charles's law,  $V \propto T$ , when  $P$  is constant.

Hence, when both  $T$  and  $P$  vary,  $V \propto \frac{T}{P}$ ;

$$\therefore V = R \cdot \frac{T}{P}$$

where  $R$  is a constant. This is conveniently written in the form

$$\frac{PV}{T} = R \text{ (a constant) } \dots\dots\dots (8)$$

Thus it may be stated that however  $P$ ,  $V$ , and  $T$  may vary, the quantity  $PV/T$  for a given mass of a given gas remains constant. This is a very important equation, and is known as the **Gas Equation**. By using this equation, it is a simple matter to calculate what volume a given mass of gas will occupy at any temperature and pressure, if the volume at any other temperature and pressure is given.

**Example.**—*A quantity of gas measured at  $27^\circ \text{C}$ . and a pressure of 740 mm. has a volume of 400 c.c. Find the volume of the gas at  $0^\circ \text{C}$ . and 760 mm. pressure.*

Initially,  $T_1 = 273 + 27 = 300^\circ \text{A.}$ ,  $P_1 = 740 \text{ mm.}$ ,  $V_1 = 400 \text{ c.c.}$

Finally,  $T_2 = 273^\circ \text{A.}$ ,  $P_2 = 760 \text{ mm.}$ ,  $V_2$  is unknown.

Since  $\frac{PV}{T} = R$  (a constant),  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ ;

$$\therefore \frac{740 \times 400}{300} = \frac{760 \times V_2}{273}$$

$$\therefore V_2 = 400 \times \frac{740}{760} \times \frac{273}{300} = 354 \text{ c.c.}$$

## 8. General Relation Between Pressure, Density, and Temperature

Since  $\text{Mass} = \text{Volume} \times \text{Density}$ , the density of any given mass of gas is inversely proportional to the volume of the gas. Denoting density by  $D$ , Boyle's law may then be written as

$D \propto P$  when  $T$  is constant,

and Charles's law as

$D \propto \frac{1}{T}$  when  $P$  is constant.

Hence, when  $T$  and  $P$  both vary,  $D \propto P/T$ , which may be written in the form

$$\frac{P}{DT} = \text{a constant} \dots\dots\dots (9)$$

By means of this equation, it is a simple matter to calculate the density of a gas at any temperature and pressure, if the density at any other temperature and pressure is known.

**Example.**—The density of hydrogen at  $0^\circ \text{C.}$  and  $760 \text{ mm.}$  is  $0.00009001 \text{ grm. per c.c.}$  Find the density at  $100^\circ \text{C.}$  and  $780 \text{ mm.}$

$$\text{Applying } \frac{P_1}{D_1 T_1} = \frac{P_2}{D_2 T_2},$$

$$\frac{760}{0.00009001 \times 273} = \frac{780}{D_2 \times 373};$$

$$\therefore D_2 = 0.00009001 \times \frac{780}{760} \times \frac{273}{373} = 0.0000676 \text{ grm. per c.c.}$$

## 9. A Perfect Gas

A gas for which the relation  $PV/T = R$  is absolutely true, whatever the values of  $P$ ,  $V$ , and  $T$ , is known as a *perfect gas*. None of the existing gases is perfect, though gases such as oxygen, nitrogen, hydrogen, and helium, which are liquefied only with great difficulty, behave very nearly as perfect gases for ordinary ranges of pressure and temperature. On the other hand, gases such as carbon dioxide, sulphur dioxide, and chlorine, which are liquefied easily, show wide departure from the relation  $PV/T = R$ , when the pressure is increased or the temperature is decreased.

It follows that, for a perfect gas, Boyle's law, *i.e.*  $PV = \text{a constant}$  when  $T$  is constant, is absolutely true; also that  $V$  is absolutely proportional to  $T$  when  $P$  is constant, and that  $P$  is absolutely proportional to  $T$  when  $V$  is constant. It may be proved that, for a perfect gas, the coefficient of increase of volume at constant pressure is constant for all temperatures and equal to the coefficient of increase of pressure at constant volume.

## 10. The Differential Air Thermoscope

A simple practical application of the expansion of air is embodied in the differential air thermoscope, which may be used to indicate, though not to measure accurately, changes of temperature.

*Leslie's thermoscope* (Fig. 73) consists of a bent tube terminating in two equal bulbs containing air. The tube contains a column of coloured sulphuric acid as an indicator. The quantity of air in the

bulbs is so adjusted that, when both are at the same temperature, the acid column is at the same height in the vertical tubes on each side of the horizontal part of the tube. Thus constructed the instrument is very sensitive to *difference* of temperature of the air in the bulbs; the expansion of the air in the warmer bulb depresses the column of acid nearest to it and raises the other column correspondingly. *Rumford's thermoscope* is very similar. The horizontal part of the tube is much longer and contains a short thread of alcohol, which takes the place of the sulphuric acid column and serves as index.

These instruments are graduated by experiment. The bulbs are immersed in water, and the position of the index corresponding to the same temperature in each bulb is marked on the scale. A difference of  $10^{\circ}\text{C.}$  is then established between the two bulbs and the corresponding positions of the index again marked. The difference of temperature between the two bulbs is now reversed and the positions of the index are again marked on the scales. The spaces between these two extreme marks on the scales are then subdivided as required, and the positions of the first marks are taken as the zeros of the scales. Such instruments have been used largely in the study of Radiation (Chapter XVII.).

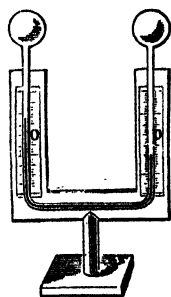


FIG. 73.

## 11. The Gas Thermometer

One of the most important applications of the expansion of gases is the use of gases as thermometric substances. Since gases expand much more than liquids, a gas thermometer is much more sensitive than a mercurial one. The expansion of any gas for  $1^{\circ}\text{C.}$  is more than 20 times that of the same volume of mercury. Further, the expansion of a gas is so great compared with that of the vessel which contains it, that it is necessary to know only the approximate law of expansion of the latter.

If a mercury thermometer is taken as the standard of temperature, there is no option but to say that mercury expands uniformly with rise of temperature, and, strictly speaking, there is no meaning in the statement. Also, if a mercury thermometer is used to give a scale of temperature, it is found that gases do not expand *absolutely* uniformly. If, however, a gas thermometer graduated

from its own indications is used, it may be said that the gas does expand uniformly with rise of temperature and also that mercury does not expand uniformly.

There is a third scale of temperature, proposed by Kelvin and referred to as the thermo-dynamic scale (Chapter XIII.) which is independent of the physical properties of any substance and in this sense *absolute*, and therefore preferable to either of the above. This scale is of the greatest theoretical importance in the more advanced study of Heat. The theory of it is, however, beyond the present stage and it is sufficient to state here that since the gas-scale of temperature agrees more closely with the thermo-dynamic scale than the mercury scale does, the gas-scale may be taken as the fundamental scale of temperature. For this reason, all temperature indicators made for practical use are graduated by comparison with a gas thermometer.

It does not matter greatly what gas is used in the thermometer so long as it is a fairly permanent gas, that is, a gas whose temperature of liquefaction is very much below the ordinary ranges of temperature. Thus air, oxygen, hydrogen, nitrogen, and helium are employed by different observers, but perhaps helium is the best one to employ on account of its chemical inactivity. Other important reasons for the adoption of air, or other gas which does not easily liquefy, as a thermometric substance will be considered later (page 127).

Theoretically, the gas thermometer may take one of two forms; any apparatus by means of which the mean coefficient of expansion at constant pressure, or the mean coefficient of increase of pressure at constant volume, of a gas has been studied may be used as a gas thermometer. For, if  $c$  be known, the relation  $V_t = V_0 (1 + ct)$  can be used to determine  $t$ , whence

$$t = \frac{V_t - V_0}{V_0 c}$$

or, the relation  $P_t = P_0 (1 + ct)$  can be used, whence

$$t = \frac{P_t - P_0}{P_0 c}$$

Thus, Regnault's apparatus (Fig. 67) forms the basis of the gas thermometer, and the methods of using this apparatus (Arts. 3 and 4) illustrate the principles of the use of such thermometers. Modern forms of this apparatus follow exactly the same principles and are illustrated diagrammatically (Fig. 74), on the left a constant

pressure thermometer and on the right a constant volume thermometer. The apparatus depicted in Fig. 71 is an example of the simple type of constant volume gas thermometer, and, generally speaking, this is the only form of gas thermometer used in practice.

Although the great expansion of a gas is in one way an advantage, it is a great inconvenience in measuring temperature by expansion at constant pressure, for the expansion is so great that a comparatively large proportion of the gas necessarily occupies, on expansion, parts of the apparatus which are not at the temperature it is desired to measure. For this reason it has been found most convenient to use the form of apparatus which measures temperature by increase of pressure at constant volume. In this apparatus

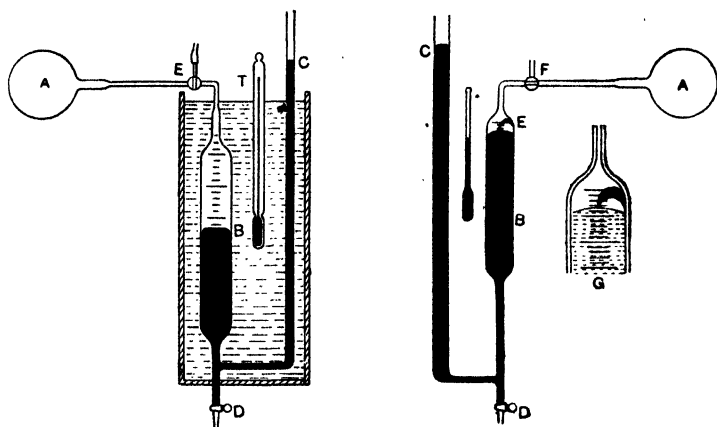


FIG. 74.

the gas can be kept throughout the experiment at the temperature it is required to measure, and this temperature is given by

$$t = \frac{P_t - P_0}{P_0} = 273 \cdot \frac{P_t - P_0}{P_0}.$$

Here  $P_t$  is known from the barometric height,  $H$ , at the time of the experiment, and the difference of level,  $h$ , of the mercury columns in the two tubes;  $P_t = H \pm h$ .  $P_0$  is determined by surrounding the bulb of the thermometer with melting ice and observing  $H$  and  $h$  in the same way as for  $P_t$ .

A constant volume gas thermometer is used for standard work on temperature and thermometry at the International Bureau of

Weights and Measures, Paris. The bulb, A (Fig. 75) is made of platinum-iridium and contains about 1 litre of hydrogen, and is connected to the manometer by a narrow metal tube, B. In the simple constant volume gas thermometer, the manometer measures only the excess of the pressure to which the gas is exposed over the atmospheric pressure, and an independent barometer must be used

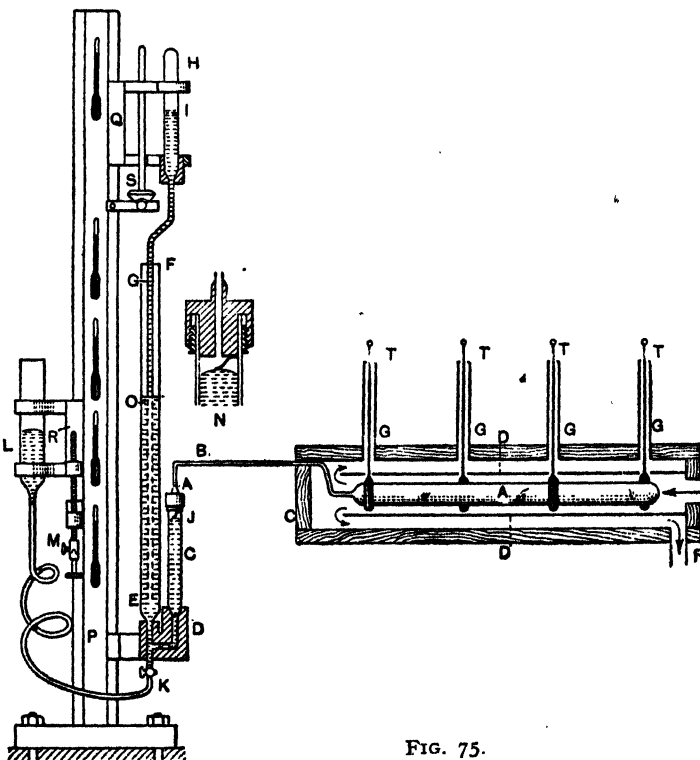


FIG. 75.

to observe the barometric height. In the standard instrument, however, the manometer and barometer are combined in a single instrument, by inserting a barometer tube, HG, in the usual manometer tube, FE. In using the instrument, the mercury is adjusted by altering the position of the reservoir, L, until the surface of the mercury is exactly in contact with the *steel* point at J. The excess pressure of the gas in the bulb over that of the atmosphere

is given by the difference of level, OJ, of the mercury columns, and the atmospheric pressure is given by the column of mercury OI. Hence, by measuring the vertical distance between the two mercury surfaces at I and J, the required pressure,  $P_t$ , is obtained.

The great difficulty in using a constant pressure gas thermometer is due to the fact that the pressure of the atmosphere is varying continuously. However, one form of such thermometer which obviates the necessity of observing and allowing for the barometric pressure and its variations has been designed by Callendar. In this instrument, the pressure of the gas enclosed in the thermometer bulb, T (Fig. 76), is maintained constantly at the same pressure as

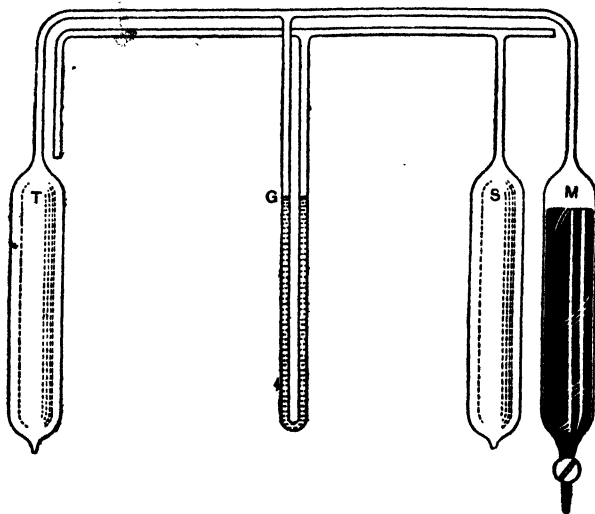


FIG. 76.

that of the gas in another exactly similar bulb, S, kept at a constant temperature in melting ice, the equality of pressure being indicated by a gauge, G, containing sulphuric acid or oil. When the gas in the bulb, T, is heated, it expands into the mercury reservoir, M and the quantity of mercury is adjusted so that the pressure in T is equal to that in S. The reservoir, M, is also immersed in melting ice, so that the temperature of the gas which overflows from T into M is maintained at  $0^{\circ}\text{C}$ . Errors due to differences of temperature of the gas in the tube connecting T and M are eliminated by having an exactly similar tube, attached to S, which is subjected to the same differences of temperature. The actual instrument (Fig. 77)



embodying the principles described can be used to measure temperatures correct to  $\frac{1}{10}^{\circ}$  C. up to about  $450^{\circ}$  C.

The thermometer is calibrated by immersing all the bulbs in melting ice, when the pressure is adjusted to equality. The bulb, T, is then heated in steam and the weight of mercury, which must be removed from M in order to equalise the pressures again, is found. Thus, temperatures are measured in terms of a weight of mercury as a fundamental interval.

Since the properties of a gas remain unchanged through a wide range of temperature, the gas thermometer may be used to deter-

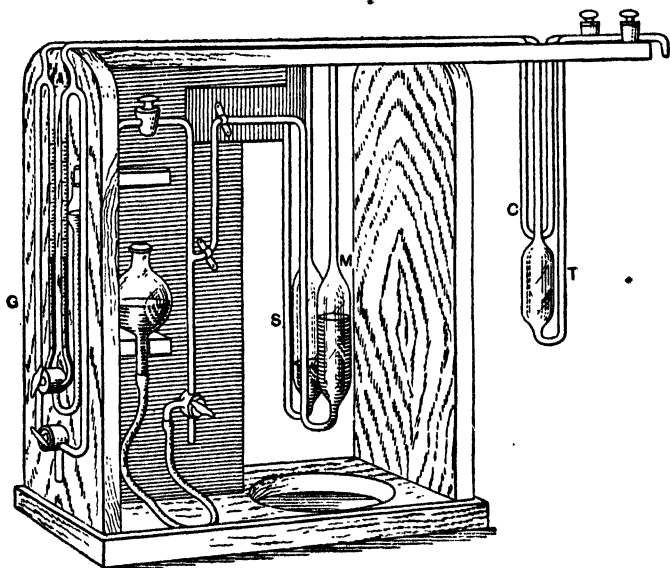


FIG. 77.

mine high or low temperatures. For ordinary temperatures, the bulb is made of glass, for moderately high temperatures of porcelain or silica, and for very high temperatures of platinum or platinum-iridium; in this last form it is a most reliable pyrometer.

The standard scale of temperature adopted for international use is "the Centigrade scale of the *constant volume hydrogen thermometer*, having as fixed points the *temperature of melting ice* ( $0^{\circ}$ ) and that of the *vapour of distilled water in ebullition* ( $100^{\circ}$ ) under the normal atmospheric pressure, the hydrogen being taken under the manometric initial pressure of one metre of mercury."

## CHAPTER VII

### CALORIMETRY. SPECIFIC HEAT

**I**N a general way the idea of *quantity of heat* is already quite familiar. A greater quantity of heat is required to heat a large mass of water from  $0^{\circ}\text{C.}$  to  $100^{\circ}\text{C.}$  than to heat a small mass through the same range of temperature: a pound of coal in burning gives out a quantity of heat which varies with the quality of the coal: the quantity of heat given out by a gas flame depends upon the quantity of gas burned per second: and so on. The meaning of the term "quantity of heat" used in this general way is well understood, but a more detailed study of the subject is necessary to decide exactly how quantity of heat is to be measured, and in what units it is to be expressed.

In this study of quantity of heat no assumption need be made as to the nature of heat. At one time heat was thought to be a weightless fluid, named *caloric*, which was able to flow from one body to a colder body. Now heat is considered to be energy, the energy of vibration and of position of the molecules of a body.

#### 1. Units of Heat

If quantity of heat is to be *measured* it is obviously essential to decide on a *unit* of measurement. The unit quantity of heat generally adopted is the quantity of heat required to raise the temperature of unit mass of water by one degree at some standard temperature. If the mass is the gramme and the change of temperature the degree Centigrade, this unit is called the *calorie*, or the *gramme-calorie*.

Unless, however, the temperature is specified the unit of heat may not be a constant, for it cannot be assumed that the same quantity of heat is required to raise 1 grm. of water  $1^{\circ}\text{C.}$  wherever that degree may be on the scale of temperature; in fact, experiment proves that different quantities of heat are required. It remains, then, to choose some particular temperature. Various proposals have been put forward at different times to fix a definite unit, but it has now been accepted internationally that the *calorie* or *gramme-calorie* be defined as the amount of heat required to raise the temperature of one gramme of water from  $14.5^{\circ}\text{C.}$  to  $15.5^{\circ}\text{C.}$

Although in accurate work it is thus necessary to define the calorie in terms of some standard temperature, yet the difference between the heat required to raise the temperature of 1 grm. of water  $1^{\circ}\text{C}$ . measured at any part of the scale and the heat required to raise the temperature of 1 grm. of water from  $14.5^{\circ}\text{C}$ . to  $15.5^{\circ}\text{C}$ . is so small that, in ordinary practice, it is quite sufficient to assume that they are identical, and to take *the calorie as the heat required to raise the temperature of 1 grm. of water  $1^{\circ}\text{C}$ .* without further reference to the part of the temperature scale. It should also be noted that, in the strictly accurate definition, the temperature is given as  $14.5^{\circ}$  to  $15.5^{\circ}$  of the International gas scale on the constant volume gas thermometer at one normal atmosphere pressure.

Other similar units to the calorie are the *pound-degree Centigrade unit* called the **Centigrade heat unit**, and the *pound-degree Fahrenheit unit* called the **British Thermal Unit (B.T.U.)**, which involve the pound as the unit of mass instead of the gramme and are used by engineers. Gas engineers have adopted as a unit of quantity the **therm**, which is equal to 100,000 B.T.U.

It will be shown later that, since heat is a form of energy, quantity of heat may be measured in energy units such as *ergs* or *foot-pounds*, and that a unit of heat may be defined without reference to any substance or scale of temperature.

*Experiment.* Take 500 grm. of water at  $0^{\circ}\text{C}$ . in a beaker and 50 grm. of water at  $11^{\circ}\text{C}$ . in another beaker. Mix the two quantities of water in the first beaker and note the final temperature, after stirring well. It will be found to be approximately  $1^{\circ}\text{C}$ . In this simple experiment the 500 grm. of water at  $0^{\circ}\text{C}$ . is raised in temperature to  $1^{\circ}\text{C}$ ., and therefore gains 500 calories. If it is assumed that there has been no loss or gain of heat in the process of mixing, the 500 calories must have been given out by the 50 grm. of water in cooling from  $11^{\circ}\text{C}$ . to  $1^{\circ}\text{C}$ . In other words, 50 grm. of water in cooling through  $10^{\circ}\text{C}$ . gives out 500 calories. This indicates that each grm. of water in cooling through each degree between  $11^{\circ}\text{C}$ . and  $1^{\circ}\text{C}$ . gives out one calorie.

If any two quantities of water at any temperatures between  $0^{\circ}\text{C}$ . and  $100^{\circ}\text{C}$ . are mixed, the final temperature, *given by experiment*, is found always to be nearly in accord with the assumption that 1 grm. of water in cooling through *any* one degree gives out one unit of heat. Hence, it may be assumed that 1 grm. of water in heating or cooling through  $1^{\circ}\text{C}$ . gains or loses one unit of heat wherever the degree be taken between  $0^{\circ}\text{C}$ . and  $100^{\circ}\text{C}$ .

**Example.**—50 gm. of water at  $10^{\circ}\text{C}$ . are mixed with 100 gm. of water at  $40^{\circ}\text{C}$ . Find the temperature of the mixture.

Let  $t^{\circ}\text{C}$ . denote the final temperature of the mixture.

The warm water cools from  $40^{\circ}\text{C}$ . to  $t^{\circ}\text{C}$ ., and loses  $100(40 - t)$  calories. The cold water is heated from  $10^{\circ}\text{C}$ . to  $t^{\circ}\text{C}$ ., and gains  $50(t - 10)$  calories.

If there is no gain or loss of heat in the process of mixing, these two quantities must be exactly equal. Thus:—

$$100(40 - t) = 50(t - 10), \text{ or } t = 30.$$

Thus, the final temperature is  $30^{\circ}\text{C}$ .

It must be noted here that in experiments of this kind it is very difficult to avoid serious errors. The exchange of heat is not confined to the two quantities of water. The vessels containing the water take a part in the exchange, and there may be considerable loss or gain of heat due to other means such as radiation. It will be explained later how these errors may be avoided to some extent, or allowed for.

## 2. The Calorimeter and its Water Equivalent

The unit of heat having been fixed, it remains to indicate how quantity of heat may be measured in terms of the selected unit. The apparatus used for the purpose of measuring quantity of heat is known as a *calorimeter*. It consists essentially of a thin metal vessel, usually of copper, brass, or silver, partly filled with water and fitted with a stirrer and accurate thermometer. The vessel must be arranged so that it is protected as far as possible from loss or gain of heat externally.

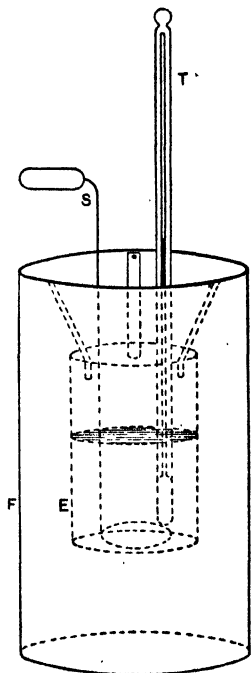


FIG. 78.

In one convenient form (Fig. 78) the calorimeter, E, capable of containing about 300 gm. of water, is suspended by threads inside a larger metal vessel, F, which protects it from external loss or gain of heat by conduction. The outer surface of E and the inner surface of F are smooth and polished, to minimise the effect of radiation. The stirrer, S, is a ring of copper wire with a vertical arm fitted with a small ebonite handle. The thermometer, T, should have its bulb well immersed in the water.

To prepare the calorimeter, a convenient quantity of water is placed in E, and the mass of the water determined by direct weighing. It is then stirred well and its temperature read immediately before proceeding to effect an exchange of heat, such as is described below and in Art. 5. When the exchange of heat is complete and the temperature of the mixture is uniform, the final temperature attained is observed.

If the mass of water is known, and the change of temperature accompanying any loss or gain of heat is observed, the quantity of heat lost or gained is easily determined. If the mass of the water in the calorimeter is  $M$  grm. and a change of temperature of  $t^{\circ}$  C. is observed, the quantity of heat gained or lost by the water in the calorimeter is  $Mt$  calories.

In the above, no account is taken of the calorimeter, stirrer, and thermometer. It is obvious, however, that these parts of the apparatus will take part in the exchange of heat, and the temperature change observed will apply to them as well as to the water in the calorimeter. Thus, the total quantity of heat gained or lost will include that gained or lost by the water and a certain unknown quantity gained or lost by the apparatus. If the apparatus is of small mass this latter quantity of heat will be small, but usually it cannot be neglected.

The simplest way of correcting for this gain or loss of heat by the apparatus is to consider that the presence of the apparatus is *equivalent* to an addition to the quantity of water in the calorimeter, and to determine the amount of this addition for any particular apparatus by experiment. *The mass to be added to the mass of water in the calorimeter as the equivalent of the apparatus in the gain or loss of heat is known as the "water equivalent of the calorimeter."*

*Experiment.* To find the water equivalent of a calorimeter.—Take a calorimeter, fill it about one-third full of water, and find the mass of the water. Stir until the temperature is uniform and observe the temperature. Add immediately a mass of water at a different temperature, sufficient to about two-thirds fill the calorimeter. Stir until the temperature of the "mixture" is uniform and note the final temperature. Then determine the mass of water added by finding the increase in the mass of the calorimeter and its contents. It is most convenient to take the water in the calorimeter at a temperature of  $30^{\circ}$  C. or  $40^{\circ}$  C. and to add water at the temperature of the room. From the data thus obtained, the water equivalent may be calculated.

**Example.**—In an experiment the mass of water first taken was 100 gm. and its temperature  $35^{\circ}\text{C}$ . The mass of water added was 110 gm. and its temperature  $15.5^{\circ}\text{C}$ . The final temperature of the "mixture" was  $25^{\circ}\text{C}$ . Find the water equivalent of the calorimeter.

Let  $x$  denote the water equivalent of the calorimeter (grammes).

The heat lost by the warm water and the apparatus in cooling from  $35^{\circ}\text{C}$ . to  $25^{\circ}\text{C}$ . was  $(100 + x) 10$  calories.

The heat gained by the cold water in being heated from  $15.5^{\circ}\text{C}$ . to  $25^{\circ}\text{C}$ . was  $110 \times 9.5$  calories;

$$\therefore (100 + x) 10 = 110 \times 9.5,$$

$$\text{i.e. } x = 4.5 \text{ gm. approximately.}$$

The value of the water equivalent obtained by such an experiment is not very accurate. *The water equivalent of a calorimeter is equal to, and is usually taken as, the product of its mass in gm. and the specific heat of the material of which it is composed* (see Art. 6).

### 3. Specific Heat

If *equal masses* of different substances take in, or give out, different quantities of heat when heated, or cooled, through the same range of temperature, the substances are said to have different *specific heats*.

The specific heat of a substance is defined as the following *ratio*

$$\frac{\text{Heat required to raise unit mass of the substance one degree in temp.}}{\text{Heat required to raise unit mass of water one degree in temp.}}$$

or since the denominator is taken as the unit of heat it can be said that the specific heat of a substance *is measured by the quantity of heat required to raise unit mass of the substances one degree in temperature*.

It should be noted that specific heat is, strictly, a *ratio*, and therefore does not have to be specified in units. Thus the specific heat of copper is 0.095. This means that 0.095 calorie of heat will raise the temperature of 1 gm. of copper  $1^{\circ}\text{C}$ ., or that 0.095 British thermal unit will raise the temperature of 1 lb. of copper  $1^{\circ}\text{F}$ ., or that 0.095 pound-degree Centigrade unit will raise the temperature of 1 lb. of copper  $1^{\circ}\text{C}$ . Similarly, 1 gm. of copper cooling  $1^{\circ}\text{C}$ . will give out 0.095 calorie of heat, 1 lb. of copper cooling  $1^{\circ}\text{F}$ . will give out 0.095 British thermal unit of heat, and so on. The specific heat of water is unity.

It is often stated that, for example, "the specific heat of copper is 0.095 calorie per gm.", but care must be taken that this does not lead to a wrong conception of the meaning of specific heat.

The following simple experiments show that the specific heats of different substances vary considerably:—

**Experiment.** Take five small spheres of iron, copper, tin, lead, and bismuth, all of the same mass, and heat them to the same temperature in a bath of water, or better, linseed oil. Remove them quickly, dry with blotting-paper, and place them on a *thick* cake of wax (Fig. 79). The wax must be thick or some of the spheres may pass through and no logical conclusion as to specific heat can be reached by the experiment. The spheres will give out heat at once to the wax, which will melt under them until they cool to the temperature at which the wax solidifies, and will sink in the wax to different depths. The order will be: iron, copper, tin, lead, and bismuth, the iron being deepest. This is the order of their specific heats.

**Experiment.** Heat 200 grm. of lead and 200 grm. of water in the same beaker. Take two other beakers, each containing 200 grm. of water at  $15^{\circ}\text{C}$ . Put the hot lead into one of these beakers and the hot water into the other. Observe the rise of temperature

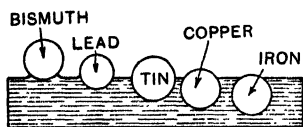


FIG. 79.

produced in each case. The rise of temperature due to the hot water will be much greater than that due to the hot lead.

If the hot water and lead were originally at  $100^{\circ}\text{C}$ ., the final temperature in the beaker to which the water is added would be about  $58^{\circ}\text{C}$ . and in that to which the lead is added about  $18^{\circ}\text{C}$ . only, *i.e.* the changes of temperature are  $43^{\circ}\text{C}$ . and  $3^{\circ}\text{C}$ . respectively. Thus 200 grm. of water in cooling from  $100^{\circ}\text{C}$ . to  $58^{\circ}\text{C}$ ., *i.e.* by  $42^{\circ}\text{C}$ ., give out about *fifteen* times the quantity of heat given out by the same mass of lead in cooling from  $100^{\circ}\text{C}$ . to  $18^{\circ}\text{C}$ ., *i.e.* by  $82^{\circ}\text{C}$ ., or approximately twice  $42^{\circ}\text{C}$ . Hence, 1 grm. of lead cooling  $1^{\circ}\text{C}$ . gives out about *one-thirtieth* of the heat given out by 1 grm. of water in cooling  $1^{\circ}\text{C}$ . Or, the specific heat of lead is about one-thirtieth that of water.

Similar experiments can be carried out using substances other than lead, and in this way rough values of the specific heat of various substances may be obtained. It should be noted that when *equal* masses of different substances at different temperatures are "mixed," the changes of temperature produced are inversely proportional to the specific heats of the substances. Thus in the preceding experiment, the change of temperature of the lead is 30 times, roughly, that of the water into which it is placed.

If  $s$  denote the specific heat of any substance, the quantity of heat required to raise  $m$  units of mass of the substance from  $t_1^\circ \text{C.}$  to  $t_2^\circ \text{C.}$  is given by  $ms(t_2 - t_1)$  units.

The *mean specific heat* of any substance for any range of temperature is measured by the average value, for that range, of the quantity of heat required to raise unit mass of the substance through one degree of temperature. Thus, if  $Q$  units of heat are required to raise unit mass of a substance from  $t_1^\circ \text{C.}$  to  $t_2^\circ \text{C.}$ , then  $Q/(t_2 - t_1)$  measures the *mean specific heat* of the substance between  $t_1^\circ \text{C.}$  and  $t_2^\circ \text{C.}$

The *specific heat of a substance at any temperature* is the mean specific heat of that substance for a very short range of temperature including the specified temperature. Thus, the specific heat of copper at  $50^\circ \text{C.}$  may be taken as the mean specific heat between  $49^\circ \text{C.}$  and  $51^\circ \text{C.}$  The shorter the range of temperature taken, the more exactly does the mean specific heat for the range give the specific heat at a definite temperature.

The *thermal capacity of a body* is given by the product of the mass of the body and the specific heat of the material.

The *specific heat per unit volume of a body* is an expression often used: it is measured by the product of the density and the specific heat of the material. This is evident since the mass of unit volume of a body is the density of the material.

#### 4. Specific Heat of a Solid by the Method of Mixtures

A very rough determination of the specific heat of a solid may be made as follows:—

(1) SIMPLE DETERMINATION.—*Experiment.* Take a piece of copper about 100 grm. in mass and weigh it. Attach a piece of thread to it and immerse it in boiling water. Set up the calorimeter as described in Art. 2, and note the temperature of the water in it. Remove the copper from the boiling water, by means of the thread attached, and transfer it as rapidly as possible into the water in the calorimeter. Stir well and note the maximum temperature reached.

**Example.**—Suppose that the data obtained in an experiment were:—

Mass of copper = 95.4 grm. and its initial temperature =  $100^\circ \text{C.}$

Mass of water in calorimeter = 200 grm. Water equivalent of calorimeter = 4 grm. Initial temperature of water and calorimeter =  $14^\circ \text{C.}$

Final temperature of water, calorimeter, and copper =  $18^\circ \text{C.}$

Let  $s$  = mean specific heat of copper between  $18^\circ \text{C.}$  and  $100^\circ \text{C.}$



Then, heat lost by copper in cooling from  $100^{\circ}\text{C.}$  to  $18^{\circ}\text{C.}$

$$= 95.4 \times (100 - 18) \times s \text{ calories} \dots\dots\dots(1)$$

Heat gained by water and calorimeter in rising from  $14^{\circ}\text{C.}$  to  $18^{\circ}\text{C.}$

$$= (200 + 4) \times (18 - 14) \text{ calories} \dots\dots\dots(2)$$

If there is no other loss or gain of heat we have—

$$95.4 \times 82 \times s = 204 \times 4;$$

$$\therefore s = 0.10.$$

In this experiment, the arrangements for heating the copper and for its transfer to the calorimeter are not entirely satisfactory. The copper may carry water with it, and it may cool appreciably during the time of transfer.

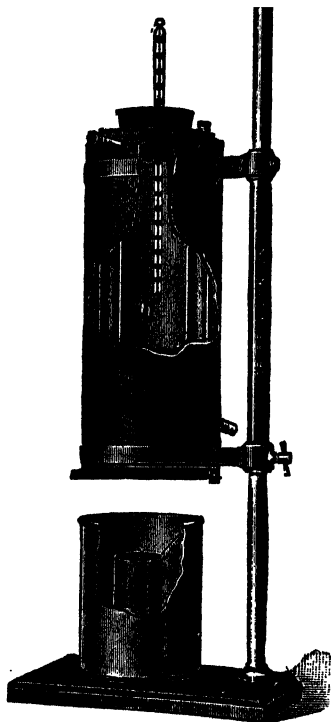


FIG. 80.

(2) **HEATER FOR SPECIFIC HEAT WORK.**—In accurate determination of specific heat, the difficulties of the simple experiment just described must be avoided and a good form of heater is necessary. Suitable apparatus can be readily obtained. The form of heater in general use consists of two concentric cylinders of copper (Fig. 80) so arranged that a current of steam from a boiler can be passed through the space between the cylinders. The interior of the inner cylinder is thus a steam oven, and objects suspended in it can be heated to nearly  $100^{\circ}\text{C.}$ , a thermometer giving the actual temperature. The method of using this heater is indicated sufficiently in the figure.

A more elaborate form of apparatus, known as **Regnault's calorimeter** (Fig. 81), is sometimes used. The calorimeter in its shielding box slides along grooves cut in the base of the framework. While the body is being heated in the steam-heater, a sliding shutter prevents transfer of heat from the heater to the calorimeter. When the body has reached the temperature of the heater, this sliding shutter is raised and the calorimeter is pushed below the heater. The body is then lowered into the water in the calorimeter without

splashing, the calorimeter is slid back quickly into its original position, and the shutter lowered. The water is then stirred cautiously, the temperature being watched during the stirring. The temperature rises quickly at first and then more slowly, becoming at length constant for a time, after which it falls gradually as the whole apparatus cools. It is this maximum temperature that is read.

(3) CALCULATION OF THE SPECIFIC HEAT. While the hot body is giving out heat to the water in the calorimeter, the calorimeter,

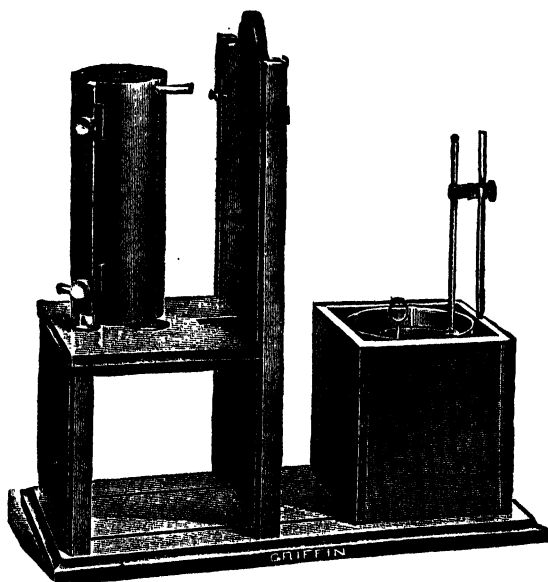


FIG. 81.

stirrer, and thermometer all receive a share. Except in very accurate work, the water equivalent of the thermometer is neglected. As the calorimeter and stirrer are usually made of copper, the specific heat of which is 0.095, their combined water equivalent is equal to 0.095 times their total mass, and this water equivalent is then considered to represent the same number of grammes of water.

To take a general case, if  $M$  grm. of a substance of specific heat,  $s$ , are heated to  $t_1^\circ \text{C.}$  and dropped into  $m$  grm. of water placed in a calorimeter of mass  $m_1$  grm. (including the stirrer), and specific heat,

$s_1$ , all at a temperature,  $t_2^\circ \text{C.}$ , and if  $t^\circ \text{C.}$  denote the final temperature, then—

Loss of heat by given substance =  $Ms(t_1 - t)$  calories.

Gain of heat by water =  $m \times 1 \times (t - t_2)$  calories.

Gain of heat by calorimeter and stirrer =  $m_1 \times s_1 \times (t - t_2)$  calories.

Hence, assuming that no heat is lost to or received from the surroundings, the loss of heat by the hot substance must be equal to the gain of heat by the water, calorimeter, and stirrer. Therefore

$$Ms(t_1 - t) = m(t - t_2) + m_1 s_1(t - t_2),$$

$$\text{i.e. } s = \frac{(m + m_1 s_1)(t - t_2)}{M(t_1 - t)}.$$

**Example.**—Find the specific heat of aluminium from the following data, obtained in an actual experiment. A piece of aluminium of mass 72.66 gm. was heated to  $100.2^\circ \text{C.}$  and then dropped into 158 gm. of water at  $10.7^\circ \text{C.}$  contained in a copper calorimeter provided with a copper stirrer, the combined mass being 89.6 gm. The final temperature was  $18.4^\circ \text{C.}$

Denote the specific heat of aluminium by  $s$ . Then—

Loss of heat by aluminium =  $72.66 \times s \times (100.2 - 18.4)$  calories.

Water equivalent of calorimeter, etc., =  $89.6 \times 0.095 = 8.5$  gm.;

$\therefore$  Equivalent total mass of water =  $158 + 8.5 = 166.5$  gm.

Gain of heat by this mass of water =  $166.5 \times 1 \times (18.4 - 10.7)$  calories;

$\therefore 72.66 \times s \times 81.8 = 166.5 \times 7.7,$

*i.e.*  $s = 0.215.$

The method described here is known as the **Method of Mixtures**. It may be used to determine the specific heat of any solid, which is not soluble in water.

#### (4) THE COOLING CORRECTION IN CALORIMETRIC EXPERIMENTS.

—It should be noted here that in all calculations from the data of calorimetric experiments, it has been assumed that there is no loss or gain of heat by the calorimeter to or from its surroundings. In all actual experiments, however, the calorimeter is subject to a small loss or gain of this kind. Although the construction of the apparatus is designed to reduce this loss or gain of heat to a minimum, it is desirable in all experiments to make a correction for this source of error. In most experiments the calorimeter is hotter than its surroundings, and the error is due to cooling during the experiments. For this reason the correction is known as the “cooling correction,” but the principle of correction is the same whether it has to be applied on account of loss or gain of heat during the experiment.

One very simple way of making the correction is due to *Rumford*. The experiment is arranged so that the average temperature of the calorimeter during the experiment is the same as the temperature of its surroundings. When this is done, the loss of heat while the calorimeter is hotter than its surroundings roughly compensates for the gain of heat while it is colder than its surroundings. To arrange this, however, it is necessary to make one or two trial experiments before proceeding with the actual determinations. Thus suppose that in a specific heat determination the temperature of the surroundings is  $14^{\circ}\text{C}$ . and that in a trial experiment a rise of  $4^{\circ}\text{C}$ . is obtained in the calorimeter. Then, in order to apply the cooling correction by Rumford's method, the initial temperature of the water in the calorimeter should be adjusted to  $12^{\circ}\text{C}$ . The highest temperature reached will then be about  $16^{\circ}\text{C}$ ., and the mean temperature during the experiment about  $14^{\circ}\text{C}$ .

Correction by this method is not quite accurate. On "mixing" the rise of temperature with time is not uniform, but the temperature rises more quickly during the first half of the increase than during the second half. The correction is therefore only approximate.

A better method is to read the temperature every quarter minute after the hot body is placed in the water in the calorimeter, until the water has passed its maximum temperature and is cooling. A graph is then plotted, showing how this temperature varies with time and from the curve obtained a fairly accurate correction may be applied.

### 5. Specific Heat of a Liquid by the Method of Mixtures

The specific heat of a liquid may also be determined by the method of mixtures. Two modifications of the method are in common use:—

(a) *Suitable for liquids which are miscible with water and which do not react chemically with water.* Place a known mass of the liquid in a beaker, raise it to a temperature  $t_1^{\circ}\text{C}$ ., pour it into the water in a calorimeter, and proceed as before. Then, if  $M$  grm. is the mass of the liquid and  $s$  its specific heat, and other quantities denoted as in the case of a solid, (page 118),

$$Ms(t_1 - t) = (m + m_1s_1)(t - t_2),$$

from which  $s$  can be found, if all other quantities are known.

(b) *Suitable for liquids which are not miscible with water, or which react chemically with water.* Place the liquid whose specific heat is required in the calorimeter. Drop into it a known mass of

solid of known specific heat and of known high temperature, and proceed as before. In this case, if  $M$  grm. of the solid of specific heat,  $s$ , at a temperature,  $t_1^\circ \text{C.}$ , are placed in the calorimeter of mass,  $m_1$  grm., of specific heat,  $s_1$ , containing  $m_2$  grm. of the liquid of specific heat,  $s_2$ , and the temperatures are  $t^\circ \text{C.}$  and  $t_2^\circ \text{C.}$  as before, then

$$Ms(t_1 - t) = (m_2s_2 + m_1s_1)(t - t_2),$$

from which  $s_2$  can be calculated.

**Example.**—100 grm. of copper of specific heat 0.095 were heated to  $100^\circ \text{C.}$  and dropped into 200 grm. of turpentine at  $15^\circ \text{C.}$  in a calorimeter of water equivalent 4 grm. The final temperature was  $23^\circ \text{C.}$  Find the specific heat of turpentine.

Let  $s_2$  be the mean specific heat of turpentine between  $15^\circ \text{C.}$  and  $23^\circ \text{C.}$

$$\begin{aligned} \text{Then, } 100 \times 0.095 \times (100 - 23) \\ = (200 \times s_2 + 4)(23 - 15), \end{aligned}$$

$$\begin{aligned} \text{i.e. } 9.5 \times 77 &= (200 \times s_2 + 4) 8, \\ \text{from which } s_2 &= 0.44. \end{aligned}$$

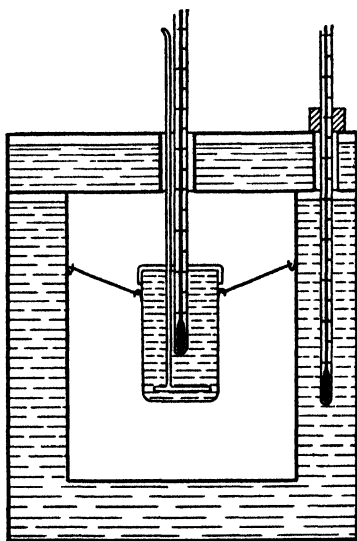


FIG. 82.

## 6. Specific Heat of a Liquid by the Method of Cooling

If a given mass of liquid at a known temperature is placed in a vessel and allowed to cool in an enclosure at a lower temperature than its own, then it is found by experiment (see page 345) that the rate of loss of heat depends only upon (1) the difference of temperature between that of the liquid and that of the enclosure, (2) the nature and extent of the surface at which cooling takes place. The heat lost is therefore independent of the nature of the liquid, so that if different liquids are allowed to cool under exactly identical conditions, as defined in (1) and (2), they will lose *heat* at the same *rate*. This is the principle of the method of cooling. The rate of *fall of temperature* will, of course, be different in each case.

To determine the specific heat of a liquid by this method, a known mass of the liquid at a temperature of about  $60^\circ \text{C.}$  is placed in a calorimeter provided with a thermometer and a stirrer. The

calorimeter is covered by a lid with small holes in it for the thermometer stem and stirrer, and the outer surface of the calorimeter is coated with lamp-black, or varnished dead black. In order to maintain the surrounding temperature constant, the apparatus is placed in the interior of a double-walled metal vessel, the space between the walls containing water at the temperature of the room (Fig. 82). The cooling which now goes on slowly is carefully watched, the liquid being stirred continuously, and the time of cooling through a given range of temperature, say from  $50^{\circ}\text{C.}$  to  $40^{\circ}\text{C.}$  is noted.

The liquid is then removed from the calorimeter and replaced by an equal *volume* of water, of known mass, raised to about  $60^{\circ}\text{C.}$  The experiment is repeated, and the time of cooling through the same range of temperature ( $50^{\circ}\text{C.}$  to  $40^{\circ}\text{C.}$ ) is noted.

Let  $m$  be the mass of the liquid and  $T$  its time of cooling from  $t_1^{\circ}\text{C.}$  to  $t_2^{\circ}\text{C.}$ ;  $m'$  the mass of water and  $T'$  its time of cooling through the same range of temperature; also let  $w$  be the water equivalent of the calorimeter, etc. Then, if  $s$  denote the specific heat of the liquid,

$$\text{Heat lost by liquid in time } T = ms(t_1 - t_2),$$

$$\text{Heat lost by calorimeter in time } T = w(t_1 - t_2),$$

$$\text{and total loss of heat} = (ms + w)(t_1 - t_2);$$

$$\therefore \text{Rate of loss of heat} = \frac{(ms + w)(t_1 - t_2)}{T}.$$

$$\text{Similarly, rate of loss of heat by water} = \frac{(m' + w)(t_1 - t_2)}{T'}.$$

But, by the experimental laws of cooling, these *rates* of loss of heat are equal;

$$\therefore \frac{(ms + w)(t_1 - t_2)}{T} = \frac{(m' + w)(t_1 - t_2)}{T'},$$

a relation from which  $s$  can be calculated.

It should be noted that the specific heat determined here is the mean specific heat for a particular range of temperature,  $50^{\circ}\text{C.}$  to  $40^{\circ}\text{C.}$ , and is relative to the mean specific heat of water for the same range of temperature. If the range of temperature is small, the method gives very approximately the specific heat at the average temperature of the range, relative to the specific heat of water at the same temperature.

**Example.**—Determine the specific heat of petroleum from the following experimental data. Mass of calorimeter = 44.6 gm., and specific heat of copper = 0.095; mass of water = 124.1 gm., mass of petroleum = 95.6 gm. Time of cooling from 55° C. to 50° C. was 410 sec. for water and 195 sec. for petroleum.

Water equivalent of calorimeter =  $44.6 \times 0.095 = 4.5$  gm.

Let  $s$  = specific heat of petroleum.

$$\text{Then } \frac{(124.1 + 4.5)(55 - 50)}{410} = \frac{(95.6 \times s + 4.5)(55 - 50)}{195}$$

$$\text{i.e. } 128.6 \times 195 = 410 \times 95.6 \times s + 410 \times 4.5;$$

$$\therefore s = 0.59.$$

A more accurate method is to observe the temperature at regular intervals of time, say every half-minute, during the process of cooling of the liquid and of the water in the calorimeter. By plotting the temperatures read in each case against time, two graphs are obtained showing the cooling over the whole temperature range covered. From these graphs the times of cooling of the liquid and of the water over a short range of temperature, say from

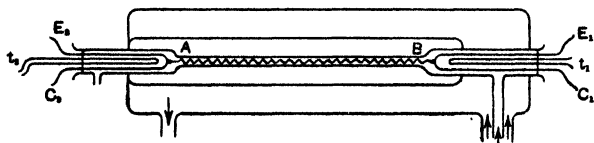


FIG. 83.

55° C. to 50° C., can be obtained, and used in the calculation. Or, the rate of cooling in each case at any definite temperature can be found by drawing tangents to the curves at the particular chosen temperature.

## 7. Specific Heat of a Liquid by the Continuous Flow Electric Calorimeter

Another method of finding the specific heat of a liquid utilises electrical heating, a steady stream of the liquid flowing through a fine glass tube being heated by a steady electric current during its passage through the tube. The method was devised by *Callendar* and used in a series of experiments by *Callendar and Barnes*.

The liquid passes through a capillary tube, AB (Fig. 83), about 2 mm. in diameter, where it is heated by a coil of platinum wire carrying an electric current. The rate of flow of the liquid can be varied, and is kept constant during a determination. The temperature of the liquid is measured as it enters and leaves the tube by

means of platinum resistance thermometers,  $t_1$  and  $t_2$ . The amount of heat supplied is obtained by measuring the electric current flowing through the wire,  $C_1 C_2$ , and the potential difference across the ends of the wire in the tube, by means of thick connecting wires,  $E_1$  and  $E_2$ . (See page 245.)

External losses of heat from the tube are reduced to a minimum by enclosing it in a glass vacuum jacket. This, in turn, is enclosed in a bath through which passes a stream of liquid from the same supply as that passing through the tube. No correction for the water equivalent of the apparatus is required, since all parts of it remain constant in temperature; observations are made only when a steady state has been reached. Any external heat loss is very small and regular, and can be eliminated by varying simultaneously the flow of the liquid and the electric current so as to obtain the same rise of temperature in the liquid for two different rates of flow.

The advantage of the method is that all conditions are steady and all the observations can be made with great accuracy. It can be used with liquids at different temperatures; the change of temperature measured is usually about  $2^\circ\text{C}$ ., so that the specific heat of the liquid at any desired temperature can be determined.

A modified form of the apparatus, for use in laboratory experiments, can be obtained (see page 247).

Several other methods of determining specific heat, which depend upon change of state and a knowledge of latent heat, will be considered later (see pages 140-144, 172-177).

## 8. The Specific Heat of Water

From the results of a number of experiments made in 1847, **Regnault** deduced that the mean specific heat of water between  $15^\circ\text{C}$ . and  $100^\circ\text{C}$ . was about 1.008 times the mean specific heat between  $10^\circ\text{C}$ . and  $15^\circ\text{C}$ . Since that time, many investigations of the variation of the specific heat of water with temperature have been made by various experimenters including *Hirn, Jamin and Amaury, Rowland, Bartoli and Stracciati, Griffiths*, and *Callendar and Barnes*, and attempts made to establish a relation showing the variation with temperature.

Callendar and Barnes measured the variation between  $0^\circ\text{C}$ . and  $100^\circ\text{C}$ ., using the continuous flow electric calorimeter (Art. 7). Taking the specific heat of water at  $20^\circ\text{C}$ ., as unity, the value was found to be 1.0094 at  $0^\circ\text{C}$ ., gradually decreasing to a minimum value of 0.9982 at  $40^\circ\text{C}$ ., was again unity at  $60^\circ\text{C}$ . and increased to



1.0074 at 100° C. From these results, the specific heat of water at any temperature,  $t^{\circ}$  C., between 10° C. and 60° C. may be obtained from the relation,

$$s = 0.9982 + 0.0000045 (t - 40)^2.$$

It is thus very nearly constant over the range of temperature used in ordinary calorimetric experiments.

Owing to its great specific heat, water absorbs much more heat in warming, and gives out much more heat in cooling, than an equal mass of almost any other substance. This explains the value of water in hot-water systems, foot warmers, etc.

Also, land is much more easily heated or cooled than water, and, in consequence, climate is affected. The prevailing temperature of an island is between that which the land would have if the water surrounding it were absent, and that which the water would have if the land were absent. Thus in summer, when the sun is above the horizon for a considerable time, the temperature of an island is lower than that of a continent; and in the winter, when the sun is above the horizon for a short time only, the temperature of an island is higher than that of a continent. Thus, the climate of an island is much more equable than that of continental countries in the same latitude.

## 9. Specific Heat of Gases

It should be noted first that a gas has two specific heats, according as it is heated at constant pressure and allowed to expand, or at constant volume without expansion. The two specific heats are referred to as the *specific heat at constant pressure*, denoted by  $s_p$ , and the *specific heat at constant volume*, denoted by  $s_v$ .

The specific heat at constant pressure is greater than the specific heat at constant volume because, not only has the temperature of the gas to be raised by the heat supplied to the gas, but in addition a quantity of heat equivalent to the work done during the expansion against the external pressure has to be supplied to the gas (see page 240).

*Regnault* made careful determinations of the specific heat at constant pressure of various gases, using the method of mixtures. The gas was collected in a reservoir, V (Fig. 84), and then heated to a high temperature by passing it through a long spiral tube immersed in an oil-bath, E. It then passed through a calorimeter, C, where it was cooled to the temperature of the surrounding water, and then escaped into the air through the tube, D. The rise

of temperature in the calorimeter was observed, and the mass of gas which had passed through was determined by the change of pressure in the reservoir, indicated by the manometer, M. The flow of gas was controlled and kept steady by a valve, R.

By equating the loss of heat by the gas to the gain of heat by the calorimeter and the contained water, the specific heat was found. Since the temperature of the calorimeter gradually rose during the experiment, the first traces of gas experienced a larger

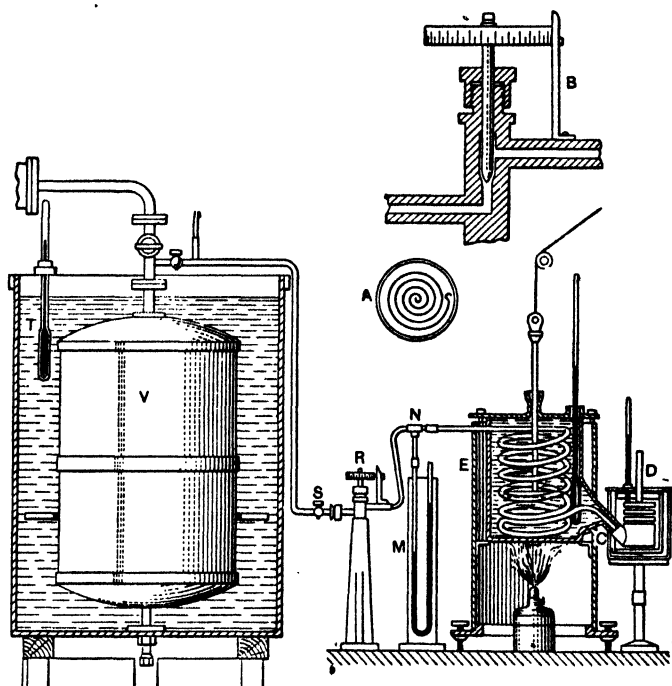


FIG. 84.

fall in temperature than the last traces, and therefore the average fall in temperature was used in calculating the loss of heat by the gas. Thus, if  $t^{\circ}\text{C.}$  was the temperature of the incoming gas, and  $t_1^{\circ}\text{C.}$  and  $t_2^{\circ}\text{C.}$  the initial and final temperatures of the calorimeter and its contents, the average fall in temperature was  $\frac{t - \frac{1}{2}(t_1 + t_2)^{\circ}\text{C.}}$  Then, if  $m$  denote the mass of gas,  $M$  the mass of water in the calorimeter, and  $w$  the water equivalent of the calorimeter,

$$ms_p [t - \frac{1}{2}(t_1 + t_2)] = (M + w)(t_2 - t_1).$$

Regnault established the following results: (1) The specific heat of a gas at constant pressure is the same whatever that pressure may be. (2) All simple gases of similar molecular structure have, at the same pressure, the same thermal capacity per unit volume. (3) The specific heat at constant pressure of a gas is the same at all temperatures.

*Callendar* and others determined the specific heat at constant pressure of gases by the continuous flow electric calorimeter (Art. 7) method. The principle of the method was exactly the same as in the case of liquids, but the apparatus was modified slightly. A steady stream of the gas was made to pass through the tube, A (Fig. 85), its temperature being observed by the platinum thermometer,  $T_1$ . After passing through the spiral tube, B, the gas passed a coil of platinum, H, heated by a known steady electric current. The gas then passed through wire gauze screens, D, to make the temperature of the gas uniform, and its temperature was again

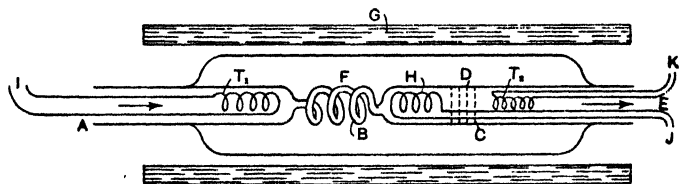


FIG. 85.

measured by the platinum thermometer,  $T_2$ . In this case also, external losses of heat were reduced to a minimum by surrounding the central tube by a vacuum jacket, F; this in turn was surrounded by a water bath, G, the water being kept at the same temperature as the gas entering the calorimeter.

The determination of the specific heat at constant volume of gases will be described later (page 175).

## 10. Properties of a Typical Thermometric Substance

This question can be considered now more fully than in Chapter II. Assuming that it is desired to indicate change of temperature by change of volume, the chief properties for a typical thermometric substance are:—

(1) *Uniform expansion with increase of temperature.* This implies the existence of an absolute scale of temperature, which does not depend upon the physical properties of any thermometric substance.

(2) *A large coefficient of expansion.* The increase of volume for  $1^{\circ}$  rise of temperature should be sufficiently large to be capable of accurate measurement.

(3) *Low thermal capacity per unit volume.* When this is the case—together with (2)—the thermometer is very sensitive to loss or gain of heat.

(4) *Constant specific heat at all temperatures.* A substance possessing this property would lose or gain equal quantities of heat for each degree change of temperature. For most substances, the specific heat increases with temperature.

(5) *The range of temperature, within which the above properties remain unchanged, should be as wide as possible.*

(6) *Its power of transmission of heat, by convection or conduction (see Chapters XV. and XVI.) should be great.* This ensures rapid and uniform distribution of temperature throughout the substance.

The only substance possessing the above properties to the required degree is air, or one of the gases which follow Boyle's law closely. For this reason, the gas thermometer is the most perfect instrument of its kind. The properties of mercury, between  $0^{\circ}\text{C.}$  and  $100^{\circ}\text{C.}$ , very closely conform to those given above. In the case of a gas thermometer, (3) and (4) above apply much more to the bulb of the thermometer than to the gas inside, for the bulb has much the larger water equivalent.

## K. Atomic Heat

As the result of a series of researches, *Dulong and Petit* in 1818 established the law that the specific heat of an element in the solid state is inversely proportional to its atomic weight. This important generalisation may be stated in an equivalent form by saying that *the product of the specific heat of an element and its atomic weight is constant*, the value of the constant being about 6.4. This product is known as the **atomic heat** of the element. Since, then, the thermal capacity of the atomic weight in grammes of any element is a constant, and since quantities equal to the atomic weight in grammes of any of the elements contain the same number of atoms, it follows that *the atoms of the elements in the solid state have the same thermal capacity.*

The values of the atomic heat (see Table VII., page 396) are somewhat variable, ranging from 5.7 to 6.8.\* This is only to be expected, however, because the specific heat of a substance is a complex quantity, the heat supplied being used not only to raise its temperature, *i.e.* to increase the vibratory movements of its molecules, but also to supply the energy necessary to force the molecules to greater distances apart, and, in the case of some substances such as iron, to supply part of the latent heat of fusion which, in those substances that pass through a viscous condition (see page 133), begins to be absorbed at temperatures far below that which is usually taken as the melting point. Moreover, in making comparisons, the specific heat should be taken, as far as possible, under similar conditions for the different substances compared. This condition can be said to be scarcely fulfilled when, in making the comparison, the specific heats of, say, lead and iron, taken at ordinary temperatures are used, for lead has a melting point of 327° C. and iron a melting point of 1500° C. So that, all things considered, the agreement is as close as can be expected.

The elements carbon, silicon, and boron were long considered to be exceptions to the general law, their atomic heats being 2.8, 4.4, and 2.3 respectively. *Weber* considered that the specific heats of these substances had not been determined under proper conditions and investigated the variation with temperature of the specific heat of each of them. It was found that as the temperature was raised, the specific heat in each case approached a limiting value, which gave for the atomic heat a close approximation to the mean value 6.4.

Research work on the atomic weight of beryllium has shown that the specific heat of this metal also increases to a limiting value with rise of temperature, and illustrates the importance of this fact in any application of the law of atomic heat to the determination of atomic weight.

**Example.**—*The atomic weight of uranium has been shown by chemical analysis of the chloride of uranium to be a multiple of 60. The specific heat of uranium is 0.028. Find the atomic weight.*

Taking 60, 120, 180, 240 as possible values of the atomic weight, the atomic heats are found to be 1.68, 3.36, 5.04, 6.72. It is evident that the correct atomic weight is 240.

It is interesting to note that the specific heat of solid hydrogen has now been determined directly, and has been found to be equal to 6. This is approximately the value necessitated by Dulong and Petit's law.

\* The average value for 32 elements being 6.4.

## 12. Molecular Heat

An extension of Dulong and Petit's law to compound molecules was investigated by *Neumann*, and later by *Kopp*, *Regnault*, and *Woestyn*. Calling the product of specific heat and molecular weight the molecular heat, it was shown that in many cases the molecular heat of a compound was equal to the sum of the atomic heats of its constituent atoms.

This may be used as a means of finding the specific heat of an element in the solid state which cannot readily be determined directly. Thus, if the molecular heat of potassium chloride is known and the atomic heat of potassium is subtracted therefrom, the atomic heat of chlorine is obtained. Dividing this by the atomic weight of chlorine, the specific heat of chlorine in the solid state is obtained.

## CHAPTER VIII

### THE LOWER CHANGE OF STATE

ATTENTION has already been called to the fact that most substances may exist in three states—solid, liquid, and gas—the application or withdrawal of heat being all that is necessary to change the state of the substance. Thus water, for example, is converted into the gaseous state by a sufficient application of heat and into the solid state by a sufficient withdrawal of heat.

#### 1. Liquefaction and Solidification

The temperatures at which the above changes take place for different substances are widely different, and in some substances the available means of producing heat and cold are too limited to effect the changes. Thus, iron changes to the liquid state at a very high temperature, platinum at a still higher temperature, and although carbon has been somewhat softened it has not been brought to the liquid state. On the other hand, many gases are brought to the liquid state only at very low temperatures and to the solid state at much lower temperatures, and it is only in comparatively recent years that these changes have been effected in the so-called permanent gases, oxygen, nitrogen, air, hydrogen, helium, etc. Although the range of observation is thus somewhat limited by the means of producing heat and cold, yet there is sufficient, and continually increasing evidence that every elementary substance exists in three states—the solid, liquid, and gaseous—though the temperature corresponding to any particular state is very different for different substances.

When a substance is spoken of as a solid, liquid, or gas, its condition at ordinary temperatures is referred to.

In this chapter, the change from solid to liquid, and its reverse, the change from liquid to solid, will be dealt with. When a solid substance changes, on heating, from the solid state to the liquid state, the process of change is known as *liquefaction*, or *fusion*, or *melting*. On the other hand, when a liquid substance, on cooling, changes from the liquid state to the solid state, the process of change is known as *solidification*, or *freezing*.

## 2. Temperature and Change of State

Experiment shows that the process of liquefaction, or of solidification, obeys a definite law with regard to the temperature at which it takes place. The law may be stated as follows: **During the liquefaction of a substance the temperature remains constant at a fixed temperature, which is different for different substances.** This temperature for any substance is known as the **melting point** of that substance.

*Experiment.* Fill a large beaker with small pieces of ice or ice shavings and insert a thermometer. The temperature is  $0^{\circ}\text{C}$ . Heat and stir so as to secure uniformity of temperature. The thermometer shows no change of temperature until the *whole* of the ice is melted. That is, during the change of state from a solid—ice—to a liquid—water—there is no change of temperature (although heat is being supplied all the time) until the change of state is complete, and during the change the solid and liquid are at the same temperature. If this experiment is repeated a number of times, it is found that the change of state always takes place at the same temperature.

If after a solid is melted the heating is still continued, the temperature of the liquid rises in the usual way.

If a liquid is cooled until the substance assumes the solid state, the temperature changes during cooling, and solidification is found to be an exact reversal of the changes observed during heating and liquefaction. That is, the temperature falls until solidification begins, remains constant at a fixed point until solidification is complete, and then falls in the usual way. Also, the constant temperature of solidification is observed to be exactly the same as the constant temperature of liquefaction. This temperature for any substance is sometimes called the **freezing point** of that substance. The *freezing point* is identical with the *melting point*.

## 3. Change of Volume During Change of State

As a general rule, most substances expand in the process of melting and contract on solidification. In the case of phosphorus the expansion on fusion amounts to 3.4 per cent., sulphur 5 per cent., and stearic acid 11 per cent. This accounts for the fact that when any of these substances are cast in glass tubes, they contract away from the glass and easily fall out when solid. But a few substances, such as *water*, *cast iron*, *bismuth*, and *antimony* contract on melting and expand on solidifying.



*Experiments.* (a) Fill a glass bulb with water and seal with a blowpipe. Place the bulb in a freezing mixture (page 145), so that the water in the bulb freezes. The bulb is burst, thus showing that the ice formed is appreciably greater in volume than the water. In this case, therefore, there is an *increase* of volume in changing from the liquid to the solid state.

(b) Melt some paraffin wax and pour it into a beaker. When it solidifies the surface will show a considerable depression, indicating that the volume of the solid wax is appreciably less than that of the liquid wax. In this case, therefore, there is a *decrease* of volume in changing from the liquid to the solid state.

(c) Nearly fill a small flask with small pieces of ice, and add water to fill the interstices of the ice. Mark the water level near the top of the neck of the flask. Then, melt the ice by heating gently, and note the gradual fall in the water level.

The **expansion of water on freezing** amounts to approximately 9 per cent., so that 11 volumes of water at 0° C. become about 12 volumes of ice at the same temperature. Consequently ice floats in pure water with about  $\frac{1}{12}$  of its volume above the surface. If water contracted on freezing, the ice as it formed would sink to the bottom, thus exposing a fresh layer of water to the cold air, and a spell of cold weather would convert rivers, lakes, and pools into solid blocks of ice.

If water is confined in a closed space, it exerts great force by its expansion on freezing, and thus in *the process of freezing* bursts water bottles and pipes. In the case of pipes, however, the damage does not become *apparent* until a thaw melts the plug of ice which has been forced into the rent, and so allows the water to escape. Boys has suggested that exposed water pipes should be elliptical in cross-section. A circle is the plane figure which for a given perimeter has the maximum area. If therefore a pipe of elliptical cross-section is subjected to internal pressure, it may accommodate itself to the pressure by altering its shape of cross-section to circular.

Much damage is done to brick and stone work by similar means. Rain or moisture from the earth penetrates the bricks or stones, and on freezing forces the particles asunder. After a thaw, the face of the wall shows evident signs of the destruction. On the other hand, the action of frost benefits the farmer by breaking down the rough clods left by the plough into a fine seed bed. Indeed,

the origin of the soil from the subjacent rock is largely due to long continued action of this kind.

A lump of cast iron floats on the liquid metal in the same way as ice on water, and an iron casting owes its sharpness of outline to the expansion which takes place on solidifying and which forces the metal into intimate contact with every part of the mould. A casting in copper or silver is much less sharp, because these metals contract on solidifying.

#### 4. Viscous State During Fusion

Most substances change from the solid to the liquid state quite sharply and abruptly, the change of state being sharply defined. For such substances, the melting point is fixed and definite and characteristic of the substance. A number of substances, however, solid at ordinary temperatures, such as glass, iron, sealing-wax, pitch, etc., pass through an intermediate *viscous* state and the change from solid to liquid is gradual. Similarly, a number of substances, liquid at ordinary temperatures, such as glycerin, acetic acid, alcohol, and other organic acids and oils, pass through an intermediate viscous state in changing from the liquid to the solid state. For all these substances, the melting point is indefinite, for the process of change of state really extends over a range of temperature which varies with the substance.



FIG. 86.

#### 5. Determination of the Melting Point of a Substance

The method of determining the melting point of a given substance depends on the nature of the substance. Simple methods which are applicable where the melting point is definite and lies between  $0^{\circ}\text{C.}$  and  $100^{\circ}\text{C.}$ , and which may be used in the case of paraffin wax, naphthalene, and similar substances, will first be described.

*Experiments.* (a) Take a piece of thin-walled capillary tubing of about  $\frac{1}{8}$  mm. bore. Melt some of the substance in an evaporating dish and fill the tube with the liquid. Attach the tube by a small india-rubber band to the bulb and lower part of the stem of a thermometer (Fig. 86). Mount the thermometer so that the bulb and tube dip into a large beaker of water. Gently heat the water, stirring it all the time. The opaque solid will suddenly change to a transparent liquid; note the temperature. It is the approximate melting point. Now remove the burner and, still stirring well,

observe the temperature when the liquid solidifies. The mean of the two readings will give a result very near the true melting point. Repeat the heating and cooling several times, keeping the temperatures within  $5^{\circ}\text{C}$ .

of the melting point and making the changes of temperature more gradual.

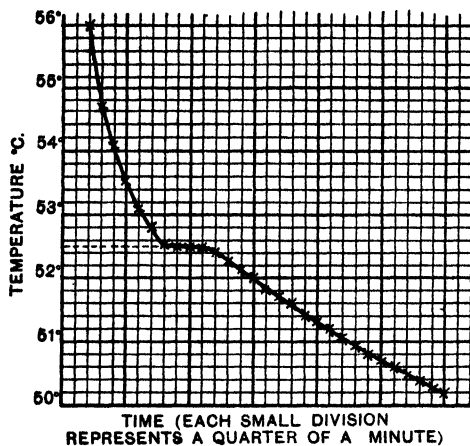


FIG. 87.

The result obtained by the above method is not very accurate. Melting and solidifying are sometimes delayed in a very narrow tube. The method is useful, however, when only a small quantity of the substance is available. Also by using a suitable bath, such as an oil-bath, the method may

be used at temperatures much higher than  $100^{\circ}\text{C}$ .

When a substance is melted and allowed to cool, the temperature falls gradually until the freezing point is reached. At this point the temperature remains steady until all the substance has solidified. After this the temperature falls once more. By observing this steady temperature, the melting point of a substance may be determined. This method (given below) is known as the *method of cooling*.

(b) Place the substance in a small copper calorimeter or glass boiling-tube, melt it, and introduce a thermometer into the liquid. Then place the vessel inside a large beaker to protect it from air currents. The apparatus used to determine specific heat by the method of cooling (Fig. 76) is very suitable for this experiment. Observe the temperature at regular intervals of time, say every quarter minute, as the substance cools. Plot a graph in which times are abscissae and temperatures are ordinates. The temperature at which the curve runs most nearly parallel to the time axis is the melting point of the substance.

This method is the most reliable one when it can be used. A typical graph obtained from an actual experiment with paraffin

wax is shown (Fig. 87), and from it the melting point is seen to be  $52.5^{\circ}\text{C}$ . If the substance is not pure, there may be more than one melting point and the curve may run nearly parallel to the time axis at two or more places. By using suitable baths and thermometers, the method may be extended to temperatures much higher than  $100^{\circ}\text{C}$ .

## 6. Influence of Pressure on the Melting Point

The influence of pressure on the melting point of a substance may be deduced from theoretical considerations, and was first stated by **Thomson**. The nature of this influence is as follows:—

(a) If a substance *contracts on melting*, as in the case of ice, increase of pressure causes a *lowering* of the melting point of the substance.

(b) If a substance *expands on melting*, as in the case of paraffin wax, increase of pressure causes a *rise* of the melting point of the substance.

*Thomson* calculated that in the case of ice, the melting point is lowered by about  $0.0075^{\circ}\text{C}$ . for one atmosphere increase of pressure. This was confirmed experimentally by his brother, *Lord Kelvin*. The apparatus used consisted of a strong glass cylinder (Fig. 88) filled with pieces of clean ice and pure water. A special thermometer, A, containing a mixture of sulphuric acid and ether as thermometric substance in order to increase the accuracy of the observations, was placed inside the cylinder. A massive ring of lead, B, kept the central portion of the thermometer free from ice so that the readings of the thermometer could be taken. The cylinder was closed by a metal cap fitted with a screw plunger, E. By rotating the screw the pressure inside the apparatus could be increased. The pressure was measured by

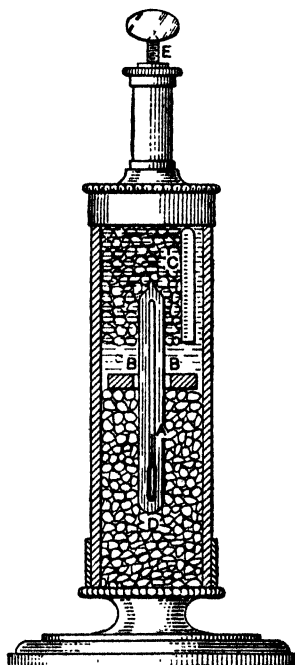


FIG. 88.

observing the compression of a volume of air contained in a tube, C, enclosed in the water in the cylinder with its open end downward. Pressures up to about 17 atmospheres could be obtained in this way.

*Bunsen* studied the effect of change of pressure on the melting point of many substances, such as wax and sulphur, which expand on melting. He used an apparatus made of glass (Fig. 89), the main body of the apparatus containing mercury. A little of the substance was placed in the short limb, E, and the long limb, AB, which was sealed at the top, contained air and served as a pressure gauge. The apparatus was placed in a water-bath and gradually heated. The mercury expanded and exerted great pressure on the substance. When the substance melted, the temperature of the water-bath was observed, and the pressure was deduced from the volume of the air in AB. By this means he found that the melting point of paraffin wax was raised from  $46.3^{\circ}\text{C.}$  to  $49.9^{\circ}\text{C.}$  when subjected to a pressure of 100 atmospheres.

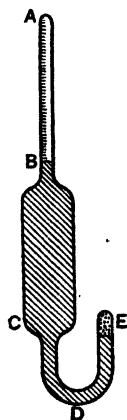


FIG. 89.

The peculiar property of ice known as **regelation** was first observed by *Faraday*, as the result of a simple experiment. Two pieces of ice were pressed together for a few seconds. On relieving the pressure, the two pieces were found frozen together at the region of contact. The pressure enabled a thin layer of the ice to melt by lowering the melting point; on relieving the pressure, the water thus formed froze again immediately.

The same process takes place when a handful of snow is squeezed in making a snowball; the outer layer becomes a shell of ice. Again, wheel-ruts over snow are coated with ice; the snow is liquefied as the wheels pass over it and the water thus formed freezes when the pressure is removed. The same process occurs in skating. The slippery nature of ice is due to the water produced by melting; very cold ice is not so slippery as ice just below  $0^{\circ}\text{C.}$  The following experiment, suggested by *Bottomley*, illustrates this same phenomenon of regelation:—

*Experiment.* Rest a solid block of ice on two supports and pass a loop of wire round the block between the supports; attach a heavy weight to the loop underneath the block. The wire gradually cuts its way through the ice, leaving, however, the block quite solid. Immediately beneath the wire, pressure liquefies the ice; the water

thus formed makes its way to a position just above the wire and freezes there.

It should be noted that, since the ice melting beneath the wire absorbs heat on melting and the water above gives out heat on freezing, the process is helped by having a wire which conducts heat easily; the heat liberated above is then conducted through the wire to assist in melting the ice below. Thus, it will be found that a copper wire works through the block more quickly than a steel wire.

Regelation is an important factor in determining the flow of glaciers. At all points where large stresses are set up in the glacier, the ice melts and freezes again as the stress is relieved. In this way stresses in the mass of the glacier are relieved as they arise and the motion of the glacier is facilitated.

## 7. Latent Heat of Fusion

It has been stated already (Art. 2) that when a substance undergoes liquefaction, or fusion, it absorbs heat during the process, without rise of temperature. Also, when a substance undergoes solidification it gives out heat during the process, without fall of temperature.

The following experiments demonstrate the above, and also illustrate the important fact—referred to as *supercooling*—that under certain conditions it is possible to cool many liquids below their freezing points before solidification sets in, the temperature rising quickly to the freezing point once solidification begins: thus water freed from air has been cooled to  $-12^{\circ}\text{C.}$ , but on dropping into it a small piece of ice solidification began, the temperature rising quickly to  $0^{\circ}\text{C.}$  This will be referred to again later.

*Experiments.* (a) Melt some crystals of sodium thiosulphate—"hypo"—in a flask. Carefully cork the flask and allow to cool. The melting point is  $45^{\circ}\text{C.}$ , but it may be cooled, if not disturbed, to the ordinary atmospheric temperature without solidifying. Remove the cork carefully and drop a small crystal of the salt in the liquid. Crystallisation occurs rapidly throughout the mass, and as the mass crystallises the heat rendered latent during the melting of the original crystals reappears and the mass becomes warm, the temperature rising to the normal melting point,  $45^{\circ}\text{C.}$

(b) Cool some water in a test-tube by surrounding it with a freezing mixture (page 145). A thermometer placed in the water

will show that the temperature falls rapidly at first, and afterwards more and more slowly, passes  $0^{\circ}\text{C.}$ , until finally, if the freezing mixture is effective, a quantity of ice suddenly forms and at the same time a sudden rise of temperature to  $0^{\circ}\text{C.}$  takes place. The water is at first cooled *below* the temperature at which freezing normally takes place, then suddenly freezing occurs, and the heat given out during the process produces the observed rise of temperature.

The heat absorbed or evolved, at constant temperature, during fusion or solidification, is called the *latent heat of fusion*. A given substance absorbs per unit mass, during fusion, and evolves per unit mass, during solidification, a definite quantity of heat which is constant for the same substance under the same conditions. The latent heat of fusion for any substance is the quantity of heat required to convert unit mass of the substance from the solid state at the melting point to the liquid state at the same temperature. Thus the latent heat of fusion of ice at  $0^{\circ}\text{C.}$  is the quantity of heat required to convert unit mass of ice at  $0^{\circ}\text{C.}$  into water at  $0^{\circ}\text{C.}$  It is also the quantity of heat given out by unit mass of water at  $0^{\circ}\text{C.}$  in becoming ice at  $0^{\circ}\text{C.}$  The latent heat of fusion of ice is often called the *latent heat of water*. The heat becomes "latent" in the water during fusion.

If the gramme is taken as the unit of mass, then the latent heat of fusion is expressed in calories per gramme. Hence, if  $L$  denote the latent heat of fusion of any substance, then the quantity of heat absorbed during the fusion, or evolved during the solidification, of  $m$  grammes of the substance is  $mL$  calories.

### 8. Determination of the Latent Heat of Fusion of Ice

The principle of the method is as follows:—A quantity of dry ice at  $0^{\circ}\text{C.}$  is placed in a weighed quantity of water, contained in a calorimeter, warm enough to melt all the ice. The temperature of the water is taken before the ice is put in and also after the ice is melted. Finally the weight of ice is found. From these data the latent heat of fusion of ice may be calculated.

Let  $M$ ,  $m$ , and  $m_1$  denote the masses of ice, water, and calorimeter;  $t_1$  and  $t_2$  the initial and final temperatures of the water;  $L$  the latent heat of fusion of ice;  $s$  the specific heat of the calorimeter. Then—

Heat given out by water and calorimeter

$$= (m + m_1s) (t_1 - t_2).$$

Heat absorbed by ice during change of state =  $ML$ .

Heat absorbed by the melted ice in rising from  $0^{\circ}\text{C.}$  to  $t_2^{\circ}\text{C.}$   
 $= Mt_2.$

Hence, equating heat given out to heat absorbed:—

$$(m + m_1s)(t_1 - t_2) = ML + Mt_2;$$

$$\therefore L = \frac{(m + m_1s)(t_1 - t_2) - Mt_2}{M}$$

As the experiment lasts an appreciable time, the cooling correction is of importance, but in this case it may be made almost negligible by adding pieces of ice until the final temperature reached is as much below the air temperature as the original temperature is above the air temperature. Care should be taken, however, that the final temperature is not so low that dew is deposited on the outside of the calorimeter.

*Experiment.* Use a calorimeter as described on page 111 (Fig. 78). Weigh the calorimeter, fill it about two-thirds full of warm water at about  $30^{\circ}\text{C.}$  and reweigh. Place the calorimeter in position and read its temperature. Break up some clear ice into convenient pieces, and, after drying each piece carefully with blotting-paper, drop it into the water. Stir well. Stop the addition of ice when the temperature is about  $10^{\circ}\text{C.}$  and when all the ice has melted stir well and take the temperature. Finally weigh; the difference in the last two weighings gives the mass of ice put into the water. Calculate the latent heat of fusion of ice as above.

*Example.*—The following observations were obtained in an experiment. Calorimeter weighed 52.94 gm.; calorimeter and water weighed 189.45 gm.; calorimeter and water and ice weighed 215.88 gm. Initial temperature,  $31^{\circ}\text{C.}$ ; final temperature,  $13.8^{\circ}\text{C.}$ ; air temperature,  $22^{\circ}\text{C.}$  Specific heat of copper, 0.095. Determine the latent heat of water.

Heat absorbed by ice in melting =  $26.43\text{ L calories.}$

Heat absorbed by melted ice in rising from  $0^{\circ}\text{C.}$  to  $13.8^{\circ}\text{C.}$  =  $26.43 \times 13.8$  calories.

Heat given out by water and calorimeter in cooling from  $31^{\circ}\text{C.}$  to  $13.8^{\circ}\text{C.}$   
 $= (136.51 + 5.03) \times 17.2\text{ calories;}$

$$\therefore 26.43\text{ L} + 26.43 \times 13.8 = (136.51 + 5.03) \times 17.2;$$

$$\therefore L = \frac{141.54 \times 17.2}{26.43} - 13.8 = 78\text{ calories per gm.}$$

The latent heat of fusion of any other substance could be found in a similar way, by putting some of the solid into some of the liquid, or some other hot liquid, and noting the fall in temperature.



In this case the specific heats of the substance in the solid and in the liquid states would be required, as well as the specific heat of any other liquid used.

The latent heat of fusion of ice at  $0^{\circ}\text{C.}$  is almost exactly 80 calories per grm. This

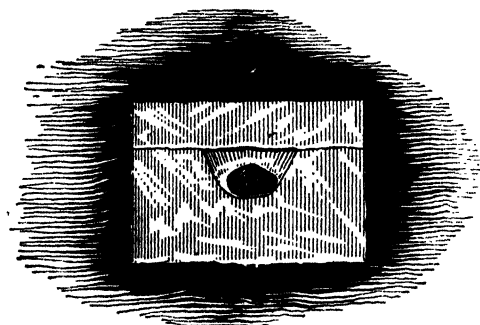


FIG. 90.

value is a comparatively large one and it is well that it is so. If the latent heat of fusion of ice were small, ice and snow on the earth's surface would melt very rapidly with rise of temperature, and disastrous floods would result; in the same way, the height of the snow-line would

increase, the distribution of glaciers would change, and portions of the earth's surface normally covered with snow or ice all the year round would be cleared during a part of the year; further, ponds and lakes would freeze very much sooner and perhaps quickly freeze solid, so that fish and other life would be destroyed.

### 9. Specific Heat Determined from Latent Heat of Fusion of Ice

When unit mass of ice at  $0^{\circ}\text{C.}$  is melted to water at  $0^{\circ}\text{C.}$ , 80 thermal units are absorbed. If, then, it is determined how much ice a known mass of any substance at an initial known temperature is able to melt, the number of thermal units it evolves in falling from its original temperature to the temperature of the ice can be calculated. From this the quantity of heat given out by unit mass falling one degree, *i.e.* the specific heat of the substance, can be obtained. There are several methods of applying this principle. The apparatus used is generally referred to as an **ice calorimeter**.

Let  $M$  be the mass of the substance,  $s$  its specific heat. It is heated to a temperature of  $t^{\circ}\text{C.}$  and then dropped into an ice chamber. In falling to  $0^{\circ}\text{C.}$ , let the mass of ice melted be  $m$ .

The heat given out by the hot body in cooling =  $Mst$  units.

The heat absorbed by the ice in melting =  $mL$  units;

$$\therefore Mst = mL, \text{ or } s = \frac{mL}{Mt}.$$

Thus, in order to calculate the heat absorbed in an ice calorimeter, it is necessary to determine the mass of ice melted with some exactness. This may be done by either of two methods: (a) by direct weighing of the water produced by the melting of the ice, or (b) by measuring the decrease in volume resulting from the change of a portion of the ice into water. In the second method, use is made of the fact that the volume of 1 grm. of ice at  $0^{\circ}\text{C}$ . is 1.0906 c.c., and the volume of 1 grm. of water at  $0^{\circ}\text{C}$ . is 1.0001 c.c., so that 1 grm. of ice at  $0^{\circ}\text{C}$ . in melting to water at  $0^{\circ}\text{C}$ . decreases in volume by 0.0905 c.c., that is, by about  $\frac{1}{11}$  of its volume, or  $\frac{1}{11}$  of the volume of water.

## 10. Ice Calorimeters

(a) **BLACK'S CALORIMETER.**—The first and simplest form of ice calorimeter was that used by *Black*, and consisted merely of a block of ice (Fig. 90). The substance whose specific heat was required, after being weighed and heated to a known temperature, was placed in a cavity hollowed out of the block.

**Example.**—A piece of brass of mass 50 grm. was heated to  $100^{\circ}\text{C}$ . and dropped into the cavity of a Black's ice calorimeter. The water produced weighed 5.9 grm.

Using the relation above, if  $s$  is the specific heat of brass,

$$50 \times s \times 100 = 5.9 \times 80; \therefore s = 0.094.$$

(b) **LAVOISIER AND LAPLACE'S CALORIMETER.**—*Lavoisier and Laplace* devised a modified form of Black's ice calorimeter. It consisted of three chambers (Fig. 91) one within the other. The innermost chamber contained the hot substance whose specific heat was required. This chamber was surrounded by a second chamber, and the space between them was filled with broken ice. A tube led from this chamber so that the water produced by the melting of the ice could be collected and weighed. To avoid heating from outside sources, a jacket of ice surrounded the second chamber. The method of using this apparatus was exactly the same as with Black's calorimeter. In both cases, some of the water produced adheres to the ice, and the results obtained are not very accurate.

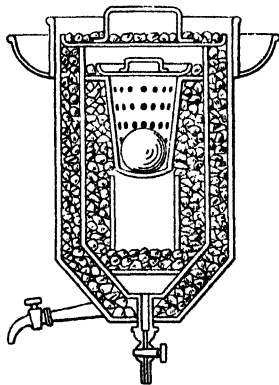


FIG. 91.

(c) BUNSEN'S CALORIMETER.—The action of this calorimeter depends upon the fact that ice contracts on melting. When 1 grm. of ice at  $0^{\circ}\text{C}$ . melts to 1 grm. of water at  $0^{\circ}\text{C}$ ., the diminution of volume amounts to 0.0905 c.c., and 80 calories of heat are absorbed. The calorimeter consists of a glass vessel, A (Fig. 92), having a thin glass tube, B, fused into it. At its lower end the vessel is joined to a bent tube, CD, which at D is fitted with a stopper carrying a piece of capillary tubing, TT. The horizontal part of this tube is calibrated carefully and carries a graduated scale, so that the volume of the tube between any two scale divisions is known accurately.

To prepare the apparatus for use the upper part of A is filled with pure, *air-free* distilled water, and the lower part and communicating tube with

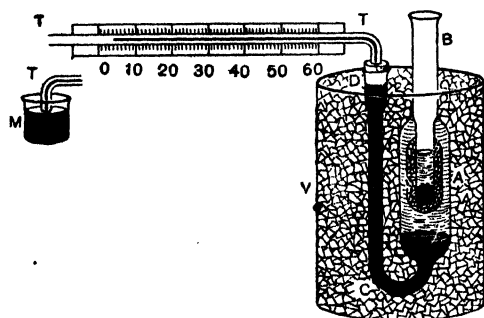


FIG. 92.

pure mercury. The instrument is then placed in a suitable vessel, V, and surrounded as completely as possible with melting ice. A current of alcohol which has been cooled by a freezing mixture of salt and ice is then passed through the tube, B, until a sheath

of ice is formed round it in the water in A. An alternative method of producing the ice sheath is by filling the tube B with solid carbon dioxide and ether. B is then cleaned out, a layer of glass-wool or sand is placed in the bottom, and a small quantity of distilled water added. The apparatus is left until all cools to  $0^{\circ}\text{C}$ . and the position of the end of the mercury column in the tube T becomes stationary. Its position is then read.

A known mass of the substance the specific heat of which is required is raised to a known temperature in a suitable heater, and then dropped carefully into B. The heat given out by this substance as it cools to  $0^{\circ}\text{C}$ . melts a quantity of ice in A; a consequent diminution of volume is produced, and is indicated by a motion of the end of the mercury column in T towards the calorimeter. When the position of this column becomes stationary a second reading is

made, and the difference of the two readings thus taken on T determines the decrease of volume caused by the melting of ice in A.

Let the decrease of volume thus determined be  $v$  c.c. Then, since the melting of 1 grm. of ice in A would produce a diminution of volume of 0.0905 c.c., the mass of ice melted in A must equal  $v/0.0905$  grm. And, as 1 grm. of ice requires 80 calories to melt it, the quantity of heat given out by the substance must equal  $80v/0.0905$ , or  $884v$  calories. But, if the mass of the substance is  $M$  grm., the temperature to which it is raised,  $t^\circ$  C., and its specific heat,  $s$ , then the heat given out in cooling to  $0^\circ$  C. is given by  $Mst$  calories. Thus:—

$$884v = Mst; \quad \therefore s = \frac{884v}{Mt}$$

This apparatus, when once put in working order, may be used to make several determinations and give accurate results, but it is troublesome to fill and prepare for use. There can be little error due to exchange of heat between the instrument and the surroundings, and in the more modern form of the apparatus this error is very much reduced by surrounding the vessel, A (Fig. 92), with a vacuum jacket.

*Example.*—5 grm. of brass at  $100^\circ$  C. were dropped into the tube of a Bunsen ice calorimeter, and the observed motion of the mercury column in the indicating tube was 54 mm. The cross-section of the bore of the tube was 0.01 sq. cm. Find the specific heat of brass.

Decrease of volume due to melting of ice =  $5.4 \times 0.01 = 0.054$  c.c.,

The melting of 1 grm. of ice causes a decrease of volume of 0.091 c.c.

Hence, a decrease of 0.054 c.c. indicates the melting of  $\frac{0.054}{0.091}$  or 0.59 grm.

The quantity of heat given out by this ice in melting  
=  $0.59 \times 80 = 47$  calories.

Hence, if  $s$  is the specific heat of brass,

$$5 \times 100 \times s = 47; \quad \therefore s = 0.094.$$

If the free end of the tube, T, is allowed to dip into mercury, M, contained in a small beaker (Fig. 92), the decrease of volume when the ice melts may be calculated from the decrease of weight of the mercury in this beaker. The tube, T, must be kept full of mercury. In this case, the scale attached to T is not required. Bunsen's ice calorimeter has proved very useful in the determination of the specific heats of substances which can be obtained only in small quantities, such as the rare metals.

It is evident that, if a substance of known specific heat is used, the apparatus may be employed to determine the latent heat of

water, or to show that ice contracts on melting, and, by measuring the contraction, to determine the density of ice. *Bunsen* made both these determinations in 1870, and found 80.02 as the latent heat of fusion of ice on the Centigrade scale, and 0.9167 grm. per c.c. as the density of ice at 0° C. The average results of later experiments for these two quantities are 79.8 and 0.9169.

## II. Nature of Latent Heat

When a piece of ice at 0° C. is heated, its temperature does not rise until all the ice has melted. What has become of the heat given to the ice?

Imagine a cannon-ball lying on the ground: it is at rest and has no destructive power. Now suppose it is flying through the air at 1000 ft. per sec.: it has an immense store of energy *because it is in motion*. Again, suppose the cannon-ball is on the very edge of a precipice, so exactly poised that the least conceivable force would dislodge it and enable it to fall: again, it has a store of energy, but this time *because it is in a particular position*—a position of advantage with regard to the force of gravity which is ready at any moment to pull it to the ground. The energy is not active at the moment under consideration, but it may become active at any moment. It may be called *potential*, latent, stored energy, or energy of position, to distinguish it from that of the moving cannon-ball, which may be called *kinetic*, active energy, or energy of motion.

Returning to the melted ice, it must be remembered that the effect of absorbed heat on a body is usually twofold. It increases the vibratory motion of its molecules, or in other words, raises its temperature, or increases its molecular *kinetic* energy. Also, it drives the molecules further apart into strained positions, from which they will return spontaneously when the temperature falls, thus increasing the molecular *potential* energy of the body. In the melting of the ice, none of the absorbed heat increases the kinetic energy: instead it is devoted wholly in forcing the molecules into new positions—positions of advantage with respect to some inter-molecular force, which will drive them back again when the absorbed heat is abstracted and the water again becomes solid.

Recent investigations by *Nernst and Lindemann*, by *Planck* and by *Einstein*, have led to the development of a theory, known as the **Quantum theory**, which has succeeded in throwing much light on this and other related problems. The basis of this theory is the conception, originated by *Planck*, that changes of energy may take

place, not continuously, but by multiples of a certain unit or **quantum**. Further discussion of the theory is beyond the scope of this book, however.

When the water freezes again, and the molecules return to their former inter-relations, the latent heat again becomes sensible, or kinetic, as vibratory motion, and thus, from the moment the water begins to freeze until the last drop is frozen, no fall of temperature takes place.

## 12. Solution. Freezing Mixtures

When a solid is dissolved in a liquid, three distinct effects are, in general, possible: (a) the physical change of state of the solid, (b) chemical combination, and (c) dissociation.

In solution, properly so called, only (a) takes place, and the process is accompanied therefore always by a fall of temperature due to the absorption of the latent heat of fusion from the solution. Thus, the solution of sodium sulphate, or ammonium nitrate, in water lowers the temperature of the solution by about  $15^{\circ}\text{C.}$ , and for this reason these solutions are often used as freezing agents.

In the majority of cases, however, chemical action takes place as well as simple solution, and there are then two thermal effects corresponding to (a) and (b) above. The changes referred to in (a) and (c) are always accompanied by absorption of heat, that of (b) always produces heat, and thus the final effect depends on whether the absorption of heat due to (a) and (c) is greater, equal to, or less than the evolution of heat due to (b).

*Experiment.* (1) Mix 4 parts by weight of sulphuric acid with 1 part of snow. A rise of temperature of about  $90^{\circ}\text{C.}$  is produced.

(2) Mix 1 part by weight of sulphuric acid at  $0^{\circ}\text{C.}$  with 4 parts of snow. The temperature falls about  $20^{\circ}\text{C.}$

A **freezing mixture** is one in which a low temperature is produced by the absorption of heat resulting from the change of state of one of the constituents of the mixture. It must be understood that the low temperature of the mixture is only temporary; it is produced *during* the change of state in the mixture, and is complete when that change of state is complete.

The simplest freezing mixtures are those already mentioned above, where the fall of temperature results from simple solution and the partial dissociation which often accompanies it. A common mixture for laboratory purposes is salt and ice, or salt and

snow. In this mixture, both constituents change state, and the temperature resulting from this double absorption of heat is  $-22^{\circ}\text{C.}$ , which is the freezing point of a definite compound of salt and water. Calcium chloride with snow or ice makes another useful freezing mixture.

### 13. Freezing Point of Solutions

The freezing point of a solution is always lower than that of the pure solvent. Thus, the freezing point of a solution of common salt in water is always lower than  $0^{\circ}\text{C.}$  It is of interest to determine how the depression of the freezing point depends upon the concentration of the solution. In carrying out such a determination, use

is made of the fact (see page 137) that a solution may be cooled appreciably below its normal freezing point before solidification occurs, and then freezing suddenly occurs and the temperature rises to its normal freezing point, where it remains for some time until gradual cooling sets in.

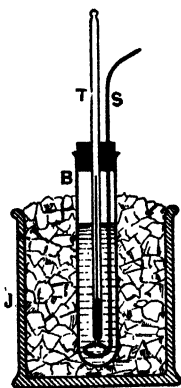


FIG. 93.

*Experiment.* To find how the depression of the freezing point of a solution of common salt in water depends upon the concentration. Fit a boiling tube, B (Fig. 93), with a cork. Through a central hole in the cork, fix an accurate thermometer, T, reading to  $\frac{1}{10}^{\circ}\text{C.}$  and the scale extending to about  $10^{\circ}\text{C.}$  below zero. Also, arrange a stirrer, S, through a second hole in the cork.

Measure 50 grm. (50 c.c.) of distilled water, and put it into the tube, B. Make a freezing mixture of ice and salt in a large vessel, J, place the tube well in the mixture, and stir the water well. Solidification gradually occurs, and as the ice crystals accumulate the temperature remains steady. Observe the temperature: it is the temperature of the freezing point of pure water.

Withdraw the tube and melt the ice. Weigh carefully 2 grm. of common salt. Dissolve this in the water, replace the tube in the freezing mixture, and stir very gently. The temperature gradually falls, passes the freezing point of pure water, is then arrested and quickly rises to a temperature just below the normal freezing point. Here it remains steady for some time while solidification occurs. Read the thermometer carefully. This gives the temperature at which pure ice separates out in the given solution.

Withdraw the tube, melt the contents, add another 2 grm. of salt, and again determine the freezing point. Repeat until about 12 grm. of salt have been added, observing the freezing point at each stage.

Calculate the depression of the freezing point for the different quantities of salt dissolved, and plot a graph between depression of freezing point and mass of salt dissolved per 100 grm. of water.

The experiment just described is used largely in Physical Chemistry for the determination of molecular weight, for *Raoult* found that the depression of the freezing point is inversely proportional to the molecular weight of the substance dissolved. To obtain accurate results, the apparatus used (Fig. 94) employs a Beckmann thermometer (page 21), the details of the method being the same as in the above experiment.

The results obtained in such an experiment in the case of a solution of common salt in water are illustrated by the curve, AP (Fig. 95). On the same graph is drawn the curve, PB, which shows the variation of the percentage solubility of salt in water over the same range of low temperatures, the solubility increasing with rise of temperature. The two curves meet at the point, P, the solubility indicated being 23.8 grm. of salt in 76.2 grm. of water, and the freezing point  $-22^{\circ}\text{C}$ . Suppose now that a solution corresponding to the point E and containing less than this quantity of salt dissolved, is cooled. The change of temperature is represented by the vertical line EF, and down to the temperature represented by F the strength of the solution remains unchanged. On further cooling, solid commences to separate, *pure ice* being formed, the remaining solution gets more concentrated and further cooling is represented by the line FP.

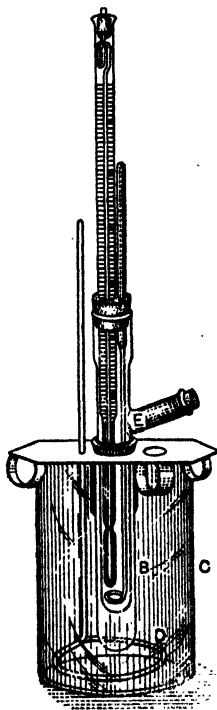


FIG. 94.



Next, suppose that a solution corresponding to the point, C, containing more than the above quantity of salt dissolved, is cooled. The change of temperature is represented by the vertical line, CD, and down to the temperature represented by D the strength of the solution remains unchanged. On further cooling, the solution contains more salt than is required for saturation, and some of the salt is deposited, the remaining solution gets weaker, and further cooling is represented by the line, DP.

Thus, whether a weak or a strong solution is cooled, when the temperature has

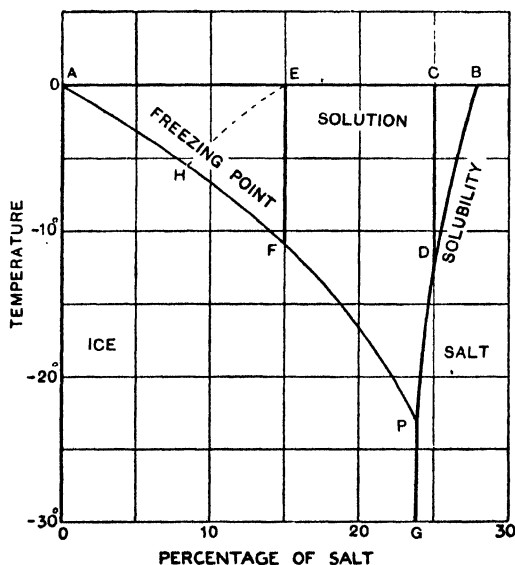


FIG. 95.

been reduced to  $-22^{\circ}\text{C}$ . the concentration of the solution which is still liquid always corresponds to the point, P, and is always 23.8 parts of salt in 76.2 parts of water. If this solution is cooled still further, both salt and ice are deposited in this constant proportion, the cooling being represented by the vertical line, PG. This constant proportion by weight of salt and ice when both are deposited together is known as the

**cryohydrate** of common salt, a definite chemical compound.

The action of a freezing mixture of ice and salt (Art. 12) can now be explained:—Suppose the mixture is first at  $0^{\circ}\text{C}$ . Ice always has a little water attached, so that some of the salt is dissolved, the state of the solution being represented by some point, such as E, above APB (Fig. 95). This solution cannot be in equilibrium with ice and some ice will be dissolved, for the state of equilibrium exists only for points on the curve, AP. The liquefaction of the ice causes a fall of temperature owing to its latent heat. Then, since excess salt is present, more salt dissolves in the solution

produced by the liquefaction of the ice. This double effect, liquefaction of ice and solution of salt, accompanied by fall of temperature, goes on until a temperature of  $-22^{\circ}\text{C}$ . is reached, corresponding to the point, P. Since at P there can be ice, salt, and solution in equilibrium, no further liquefaction of ice will take place, and therefore the temperature will not fall any lower.

#### 14. Melting Point of Metals and Alloys

By using suitable baths and thermometers, the method of cooling (page 134) may be used to determine the melting point of a

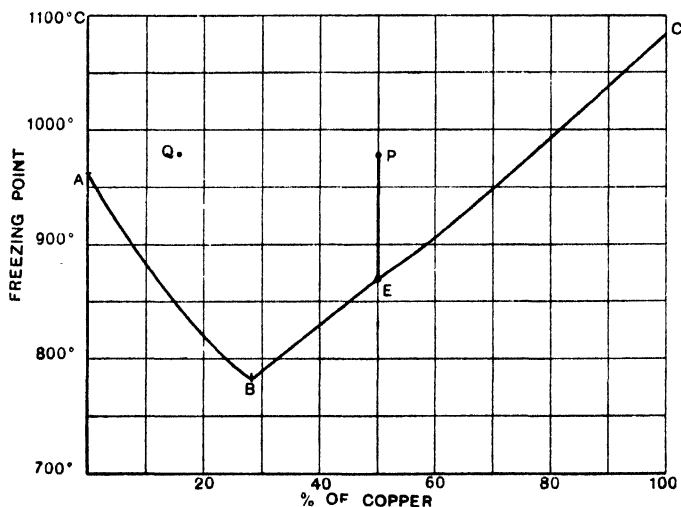


FIG. 96.

metal, and the cooling curve obtained is similar to that given by other substances, the melting point being clearly defined.

When alloys are melted and allowed to cool, the cooling curve obtained often shows more than one horizontal part, each of these marking the melting point of one of the metallic constituents, or of a stable alloy formed between two of them. Also some alloys melt at a much lower temperature than that of their constituents.

Thus, the curve, ABC (Fig. 96), gives the melting points of alloys containing different proportions of silver and copper, A giving that of pure silver and C that of pure copper. The alloy containing 28 parts of copper and 72 parts of silver has the lowest

melting point of all the alloys, as shown by the point, B. This particular alloy is known as the *eutectic*, and corresponds to the cryohydrate in ice and salt mixtures (Art. 12). If an alloy of the composition represented by P is allowed to cool, solidification will start when the point, E, is reached, but the solid formed will be pure copper, and this separation of copper will continue until the point, B, is reached, after which the eutectic will solidify, the composition remaining constant. The result is that the solid mass will consist of crystals of *pure copper* embedded in a matrix of the eutectic alloy. Similarly, if an alloy of the composition represented by Q is allowed to cool, the solid mass will consist of crystals of *pure silver* in a matrix of the eutectic.

In the case of copper-silver alloys there is only one eutectic, but in other cases, such as magnesium-tin and gold-aluminium alloys, more than one eutectic occurs, while in the case of alloy-steels the phenomena become even more complex.

The following are examples of alloys which melt at a very much lower temperature than their constituents:—(1) *Wood's fusible alloy*, consisting of bismuth, lead, tin, and cadmium in the proportions 4 : 2 : 1 : 1; it melts at 65° C. (2) *Rose's metal*, consisting of bismuth, lead, and tin in the proportions 2 : 1 : 1; it melts at 94·5° C.

Such readily fusible alloys have useful practical applications. They are sometimes used as "fuses" in electrical circuits. An essential part of the automatic sprinkler, with which large buildings are fitted in case of fire, consists of a plug of such an alloy inserted in a water pipe; if a fire occurs, the plug melts and the sprinkler operates.

## CHAPTER IX

### THE HIGHER CHANGE OF STATE

THE process of change from the liquid state to the gaseous or vapour state is known as **vaporisation**. The reverse process which takes place when a gas or vapour changes into a liquid is known as **condensation**. The general phenomena of vaporisation and condensation are closely analogous to those of liquefaction and solidification, but the subject is complicated by the fact that a liquid gives off vapour *from its free surface at all temperatures*, and also by the influence of external pressure. The process by which a liquid gives off vapour *from its free surface at all temperatures* is known as **evaporation**: this form of vaporisation will be dealt with in the next chapter.

#### 1. Vaporisation and Condensation

The elementary phenomena of *vaporisation* can be illustrated as follows. Place some distilled water in a flask fitted with a thermometer and having a side tube (Fig. 97). First arrange the thermometer so that the bulb is well immersed in the water, but not too close to the bottom of the flask. Heat the flask gently and observe the behaviour of the liquid and the readings of the thermometer.

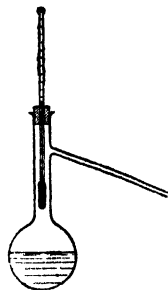


FIG. 97.

As the heating continues the temperature rises, and the vapour which is given off from the surface of the water at all temperatures is seen to condense in the neck and side tube of the flask, and to form a cloud of condensed vapour at the mouth of the tube. As the temperature rises this escape of vapour at the surface becomes more marked, and small bubbles form and escape from numerous points of the inner walls of the flask. Ultimately the temperature becomes stationary at a fixed point,  $100^{\circ}\text{C.}$ , and the liquid becomes agitated by the rapid escape of bubbles of vapour *throughout the whole mass*. The liquid is said to *boil*. If heating is continued, the boiling proceeds steadily and the liquid boils away, *i.e.* changes to water vapour or steam, but the temperature remains almost constant during the process. If the thermometer is now raised (Fig. 97)

so that the bulb is in the steam, it will be found that the temperature still remains constant at the same point. This constant temperature is called the **boiling point** of the liquid.

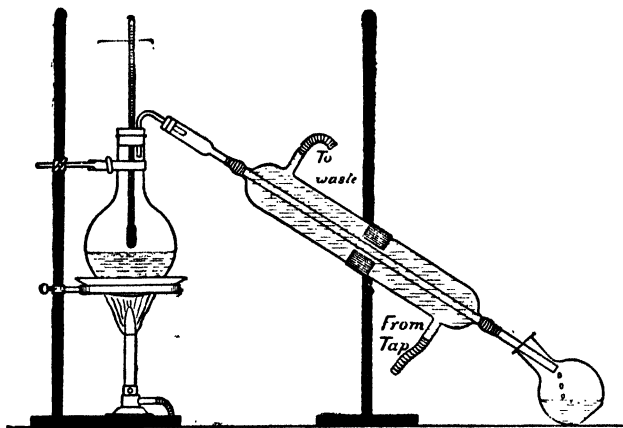


FIG. 98.

Careful observation of the process of boiling reveals that the bubbles of vapour escape through the liquid from points on the walls of the flask, and that the process is facilitated by placing a few pieces of porous earthenware, broken glass, etc., in the flask.

If the experiment be repeated with alcohol (*keep the vapour away from the flame*) the general progress of the experiment will be found to be the same as for water, but the boiling point will be found to be about  $78^{\circ}\text{C}$ .

From these experiments, it is seen that, (1) A liquid changes by *boiling* or *ebullition* from the liquid state to the vapour state at a temperature which is constant throughout the process of ebullition: this constant temperature is the *boiling point* of the liquid under the conditions of the experiment; (2) Under given conditions, each liquid has a distinctive boiling point characteristic of the liquid.

During the process of *condensation*, the phenomena of vaporisation are observed in the reverse order. The temperature at which condensation takes place is identical with the boiling point of the liquid under the same conditions, and just as a liquid in boiling at a given temperature changes to vapour at the temperature of the liquid, so a vapour in condensing gives a liquid at the temperature of the vapour. Thus, when water boils at  $100^{\circ}\text{C}$ ., the steam

produced is also at  $100^{\circ}\text{C}.$ , and when this steam condenses the condensed water, *when first formed*, is also at  $100^{\circ}\text{C}.$

In experimental work it is often necessary and useful to facilitate condensation. This is usually effected by an arrangement known as a *condenser*. The simplest form of condenser is commonly known as the *Liebig condenser* (Fig. 98), which consists of an inner tube surrounded by a wider jacket. The vapour is passed into the inner tube and a stream of cold water is passed through the jacket. The cooling effect of the water causes the vapour to condense and the condensed liquid is either run off into a receiver, or, the condenser being placed sloping upwards, allowed to run back into the vessel in which the vapour is produced. The cooling water enters at the lower end of the condenser and leaves at the higher end. Another form of condenser is that in which the vapour is condensed in a spiral tube, or *worm* (see Fig. 100), surrounded by cold water.

## 2. Change of Volume During Change from Liquid to Vapour

When any liquid boils, a large quantity of vapour is produced. In other words, when a liquid changes to a vapour there is a very great increase in volume. Thus, in the case of water the volume of the steam at  $100^{\circ}\text{C}.$  and atmospheric pressure is nearly seventeen hundred times the volume of the water from which it is produced; *i.e.* a cubic inch of water produces about a cubic foot of steam.

The graph (Fig. 99) shows the changes in volume which occur when 1 grm. of ice at  $-20^{\circ}\text{C}.$  is heated until steam is produced,

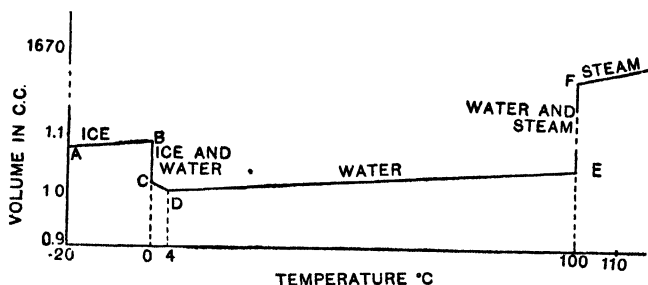


FIG. 99.

and the temperature of the steam raised to  $110^{\circ}\text{C}.$  at atmospheric pressure, 760 mm. The graph is plotted from the following data:—

TEMPERATURE (° C.)	VOLUME OF 1 GRM. IN C.C.
- 20 } Ice	1·0900
0 }	1·0906
0 }	1·0001
4 } Water	1·0000
50 }	1·0120
100 }	1·0432
100 } Steam	1672·
110 }	1716·

The line representing the change in volume of the steam is directed towards a point on the temperature axis situated at  $-273^{\circ}\text{C}$ .

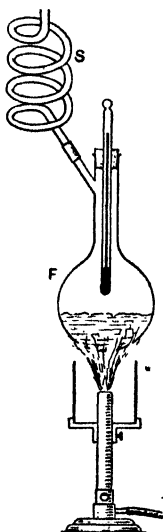


FIG. 100.

### 3. Determination of the Boiling Point of a Liquid

The determination of the boiling point of a liquid depends upon the fact that when a liquid boils and is changed into vapour the temperature of the vapour is the same as the boiling point of the liquid under the conditions of the experiment and remains constant during the process.

*Experiment.* Take a clean small flask (Fig. 11 or Fig. 12), preferably provided with a side tube, and fit an accurate thermometer through a well-fitting stopper. Place some fragments of earthenware in the flask to facilitate boiling, and then nearly half fill the flask with the liquid. Mount the flask over a Bunsen burner and heat gently until the liquid boils. When the liquid is boiling, adjust the thermometer so that the top of the mercury column in the stem is just visible above the

stopper, taking care, however, that the bulb is not immersed in the liquid. As soon as the temperature becomes steady, read it; it is the boiling point of the liquid at the pressure inside the flask. If the boiling has not been allowed to proceed too rapidly, the pressure inside the flask is equal to the pressure of the atmosphere.

The method described may be used to determine the boiling point at the existing atmospheric pressure of various liquids such as ether, alcohol, turpentine, etc. (see Art. 4). In some cases it is undesirable to allow the vapour of the liquid to escape into the atmosphere, and to prevent this the side tube of the flask may be

connected to a long piece of open spiral tubing, S (Fig. 100), in which the vapour may condense and flow back into the flask. Or, the flask may be joined to a condenser (Fig. 98). If the liquid is available only in very small quantity, the flask may be replaced by a test-tube (Fig. 101).

#### 4. Influence of Pressure on the Boiling Point of a Liquid

The quantity of liquid, the size of the flask, the rate of heating may all be changed without causing any appreciable change in the boiling point of the liquid. The material of the flask has a slight effect on the temperature of the boiling liquid, but none on the temperature of the vapour arising from the boiling liquid. But, a change in the pressure to which the surface of the liquid is exposed makes a material change in the boiling point. This fact is illustrated by the following simple experiment, due to **Franklin**:—



FIG. 101.

*Experiment.* Boil some water in a round-bottomed flask until all the air is expelled, and its place taken by water vapour. Remove the source of heat, cork the flask tightly, and arrange the flask in an inverted position (Fig. 102). Allow the flask to cool in this position until boiling ceases entirely. Then pour some cold water over it. It will be found that the water again begins to boil vigorously and may be made to do so for some time.

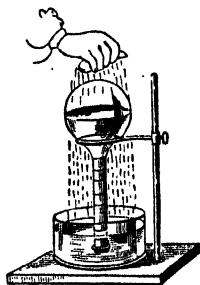


FIG. 102.

The cold water causes the water vapour in the space over the water to condense; the pressure on the surface of the water is decreased by this condensation. It is evident that the boiling point of the water is lowered, for the temperature was below  $100^{\circ}\text{C}$ . before the cold water was poured over the flask, and the final temperature is therefore well below  $100^{\circ}\text{C}$ . Similarly, the boiling point of any liquid at pressures below that of the atmosphere is lower than the boiling point under normal pressure.

If the pressure is increased above that of the atmosphere, the boiling point of a liquid is higher than the boiling point under



normal atmospheric pressure. This may be shown by using **Marcet's boiler**, an apparatus designed specially for this purpose. The apparatus consists of two stout brass hemispheres (Fig. 103) securely bolted together. The lower hemisphere contains a quantity of mercury, and a quantity of water. The upper hemisphere is fitted with a tap, and two projecting outlet tubes. Into one of these is fitted securely a thermometer, and into the other a strong glass

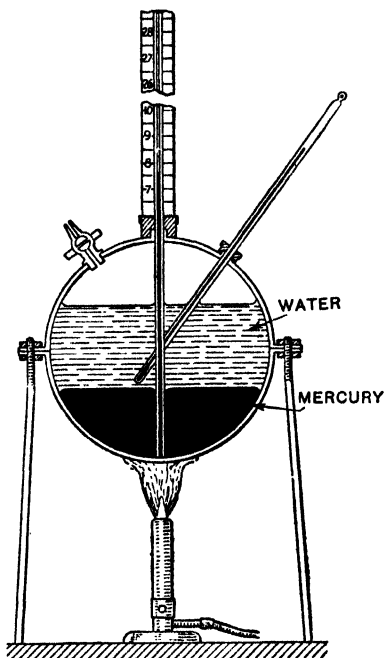


FIG. 103.

tube which passes below the surface of the mercury in the lower hemisphere. This tube is about 30 inches in length and a scale attached to it is graduated, usually in inches, to show the height above the surface of the mercury. The boiler is mounted on a tripod stand. The boiler is heated by means of a Bunsen burner, starting with the tap open. The water boils and the thermometer indicates the boiling point under the existing atmospheric pressure. On closing the tap, the pressure inside the boiler increases, the mercury rising in the central tube to indicate the excess pressure above that of the atmosphere. At the same time the thermometer shows that the boiling point of the water is raised as the pressure is increased. The pressure may be increased to

about twice that of the atmosphere, when the boiling point of water will be about  $120^{\circ}\text{C}$ .

There is considerable danger in experimenting with boiling under pressures much greater than the atmospheric pressure, particularly with glass vessels, but for pressures less than the atmospheric pressure, the boiling point of a liquid for a number of measured pressures may be determined safely and conveniently by using the apparatus shown in Fig. 104. A flask, **F**, is connected through a

condenser, G, to a large flask, R, which communicates with a U-tube mercury manometer, M, by a tube, A, and with a pump by a tube, B, which is provided with a good tap, C. R is kept in a bath of cold water; it serves to keep the pressure constant during observations and also to introduce a large volume of air into the apparatus. The liquid under observation is placed in the flask, F, and the pressure under which it is made to boil is adjusted by means of the pump and measured by the manometer, M. An accurate thermometer, *t*, fitted into F so that its bulb is immersed in the vapour of the liquid, gives the boiling point corresponding to each pressure. The vapour produced during boiling condenses in G and the condensed liquid runs back into the flask, F. The

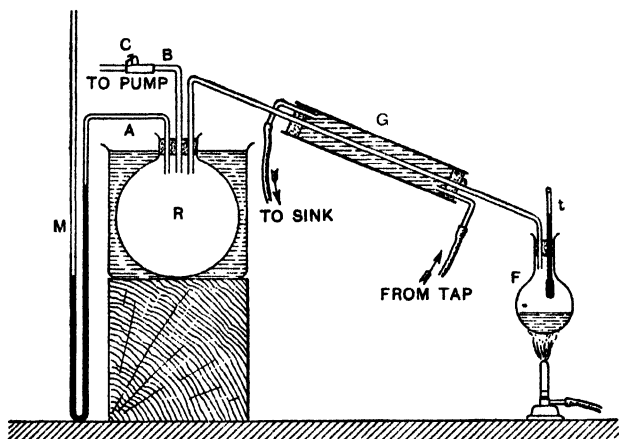


FIG. 104.

pressure at any time is obtained by observing the difference in height of the mercury columns in the manometer, M, and subtracting this from the barometric reading at the time of the observations.

The flask is half-filled with the liquid and is heated gently until the liquid boils. When the reading of the thermometer is stationary, the temperature is taken and the heights of the manometer columns are read simultaneously. By means of the pump, the pressure in the apparatus is diminished until the manometer columns show a difference in level of about 10 cm. and the boiling point is observed again. This process is continued until a number of readings of boiling points and their corresponding pressures are obtained.

**Example.**—The following readings were obtained in the case of water by using such an apparatus:—

BOILING POINT	PRESSURE IN MM. OF MERCURY
96° C.	657
92° C.	567
88° C.	486
81° C.	370
74° C.	276
67° C.	204
59° C.	142

By using a metal boiler instead of the glass flask, F, and pumping air into R to increase the pressure, instead of withdrawing it, the boiling point can be observed for pressures greater than that of the atmosphere.

*Regnault* used metal vessels in a form of apparatus similar to that just described in his investigation on the pressure of water vapour for temperatures above 100° C. (see page 183 and Table XV., page 398).

*The boiling point usually assigned to a liquid is the temperature at which ebullition takes place under the normal pressure, which is equal to that due to 760 mm. of mercury at 0° C. at sea-level in latitude 45°.* The latitude and height above sea-level of the place of observation must be given because the pressure due to a liquid column is equal to the product of the height of the column, the density of the liquid, and the acceleration due to gravity. The last factor depends on the latitude and height of the place of observation. If  $\lambda$  is the latitude and  $h$  the height in *feet* of the place of observation above sea-level, it has been shown that the normal pressure expressed in mm. of mercury at 0° C. is:—

$$760.000 + 1.94562 \cos 2\lambda + 0.0000455h.$$

**Example.**—For South Kensington,  $\lambda = 51^\circ 30'$ , and  $h = 50$  ft., hence the normal pressure is—

$$\begin{aligned} 760.000 + 1.94562 \cos 103^\circ + 0.0000455 \times 50 \\ = 759.56 = 759.6 \text{ mm.} \end{aligned}$$

This means that a mercury column at South Kensington, 759.6 mm. in height, exerts a pressure equal to that exerted by a column 760 mm. in height in latitude 45° at sea-level. Hence, the boiling point of water is 100° C. in South Kensington when the barometer, corrected for temperature, reads 759.6 mm.

### 5. Practical Applications

The change of the boiling point of a liquid with change of pressure has many practical applications.

**THE HYPSONETER.**—This is used for the determination of heights, and is very convenient for this purpose because of its portability. This instrument is merely a small vessel conveniently constructed for observing the boiling point of water at any place. It consists (Fig. 105) of a small boiler heated by a spirit lamp, and is provided with a delicate thermometer which is surrounded by steam in the upper part of the vessel. The steam escapes at the top by a small side tube which communicates with the outer air, so that boiling takes place under the atmospheric pressure.

The principle of its use for such determinations is based on the fact that the boiling point depends on the external pressure, and that when the former is known the latter is determined. Hence, if the temperature at which water boils at sea-level is found, and at a place the height of which above sea-level is to be determined, by reference to a table the corresponding atmospheric pressures can be obtained, from which the required height can be calculated.

An approximate relation between altitude and atmospheric pressure is:—

$$h = 18400 (\log p_1 - \log p_2)$$

in which  $h$  is the difference in altitude in *metres* of two stations, and  $p_1, p_2$  are the normal atmospheric pressures at lower and upper station respectively. Expressing the pressures in terms of the boiling points of water, this relation becomes—

$$h = 295 (t_1 - t_2), \text{ approximately,}$$

where  $t_1, t_2$  are the normal boiling points of water at the lower and upper station respectively. If the lower station is at sea-level,  $t_1 = 100^\circ \text{C}$ . very nearly, and  $h$  is the height of the upper station above sea-level.

**Example.**—*The average value of the boiling point of water on the summit of Snowdon is  $96.3^\circ \text{C}$ . Find the height of the mountain.*

Applying the above relation,

$$h = 295 (100 - 96.3) = 1091 \text{ m.} = 3580 \text{ ft.}$$

If heated in a closed vessel, water may be raised to very high temperatures, a fact which is often of great utility in industry.

**PAPIN'S DIGESTER.**—Papin's digester is an instance of its application, which is used for the purpose of subjecting substances to the action of water at a temperature considerably higher than



FIG. 105.

100° C. It consists (Fig. 106) of a strong bronze vessel, covered by a lid secured by a screw and fitted with a safety valve, to prevent the internal pressure becoming greater than the vessel can sustain.

The fact that water boils below 100° C. at high elevations is a source of inconvenience in cooking. In such cases a modified form of Papin's digester is used. Similarly, modern "cookers" have been designed on the same principle.

Again, in the boiler of a steam engine the temperature rises considerably if the steam is not drawn off. Thus if the gauge registers 55 lb. per sq. in., the temperature within is about 150° C.

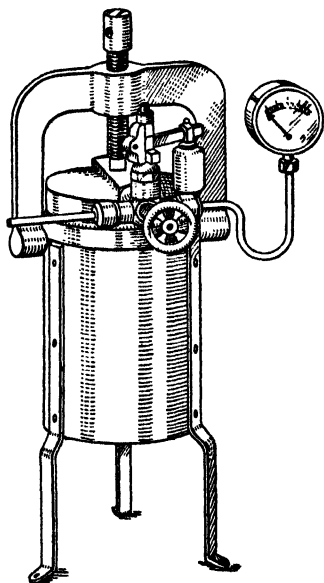


FIG. 106.

**VAPOUR JACKETS.**—One of the simplest methods of keeping a body at constant temperature is to place it in a vessel surrounded by the vapour of a liquid boiling at constant pressure. Such a chamber has already been described in the determination of specific heats (Fig. 80). If the pressure is normal, the temperature is the normal boiling point of the liquid used, but the pressure may be regulated so as to give any temperature required. For this purpose, the apparatus in general use is very similar to that shown in Fig. 103, the only difference being that the flask, F, is replaced by a boiler, into the top of which is sealed the chamber whose temperature is to be kept constant.

## 6. Boiling Point of a Solution

It was seen on page 146 that the presence of a salt in solution *lowered* the freezing point below the normal freezing point of the solvent. Similarly, the presence of a salt in solution *elevates* the boiling point. To detect this the thermometer is, of course, placed with its bulb in the solution; the temperature of the vapour given off falls quickly to that of the vapour from the pure solvent. For weak solutions the elevation is proportional to the concentration and inversely proportional to the molecular weight of the solute.

*Experiment.* To find how the boiling point of a salt solution depends on the strength of the solution.—Take a flask (Fig. 107) fitted with a cork carrying a thermometer and an exit tube which ends in a piece of india-rubber tubing closed by a screw clip. Weigh the flask, etc., when empty. Add about 15 gm. of common salt and re-weigh. Then add about 300 c.c. of water and dissolve the salt. Place the thermometer with its bulb well immersed in the solution and, the clip being open, bring the solution to the boil. Boil gently, preventing bumping by pieces of earthenware, and when the thermometer is rising very slowly read the temperature. Withdraw the flame immediately and close the clip. As the flask cools open the clip occasionally to equalise the pressure in the flask to that of the atmosphere or the flask may break. Read the barometer and calculate the true boiling point of water at the existing atmospheric pressure. When the flask is cold, weigh again and thus find the weight of water in the solution. Thus, the elevation of the boiling point for a known concentration of salt in water can be determined.

Repeat the series of observations for greater concentrations until the boiling point is about  $5^{\circ}\text{C}$ . above that of pure water at the same pressure.

Plot a graph showing how the elevation of the boiling point depends on the concentration. The concentration should be calculated in gm. of salt per 100 gm. of water. Calculate the elevation produced for a solution containing  $\frac{1}{100}$  gm.-molecule of salt per 100 gm. of water. It will be found to be about  $\frac{1}{100}^{\circ}\text{C}$ .

The most accurate apparatus for determining boiling point elevation was devised by *Beckmann*. The thermometer used is of the same type as that used to measure the depression of the freezing points of solutions (pages 21, 147). The solution is boiled in a tube, A (Fig. 108), having a platinum wire fused through the bottom, and the tube is partly filled with glass beads. This promotes boiling and prevents superheating of the liquid. The inner tube is surrounded by a wider tube, B, in which the same solution is kept boiling. Thus the amount of direct heat which has to be supplied to the inner tube is very small, and the tube is further protected by asbestos from the direct action of the flame, again to prevent

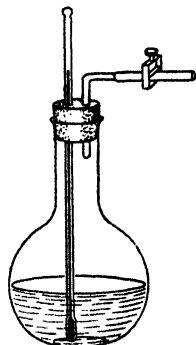


FIG. 107.

superheating. Both the inner and outer vessels are fitted with reflux condensers, C and D, which return the condensed vapour to the tube from which it emanates. With this apparatus it is possible to determine boiling points to within  $\frac{1}{1000}^{\circ}\text{C}$ . It is used in the determination of molecular weight in Physical Chemistry.

## 7. Condensation and Distillation

Distillation is a combined process of vaporisation and condensation.

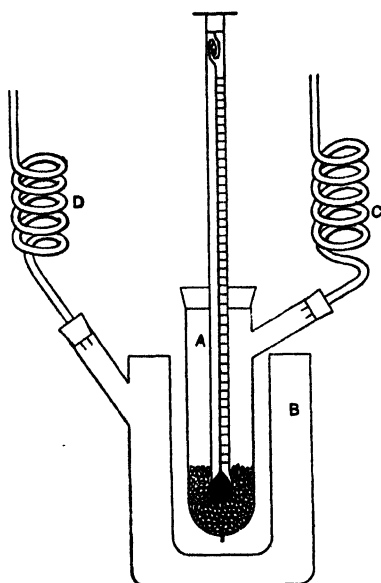


FIG. 108.

It is much used for obtaining pure or distilled water from ordinary tap water, or from salt water. It is also of frequent use for manufacturing and chemical purposes. The liquid to be distilled is heated in a suitable vessel and the vapour produced is passed through a condenser, such as a long spirally coiled tube or worm surrounded by cold water, or is, in some other way, cooled to a temperature sufficiently low to cause the vapour to condense. The liquid thus produced is collected in a vessel into which the condenser leads; it is free from all solid matter contained, either in suspension or in solution, in the original liquid. A simple form of distillation apparatus is shown

on page 152 (Fig. 98), and needs no further description.

## 8. The Spheroidal State

A peculiar phenomenon connected with vaporisation is that known as the spheroidal state. When a drop of water is allowed to fall on a hot metal plate at a temperature a little above that of boiling water, the drop boils away with a hissing noise. If, however, the plate is heated much above the boiling point of water, the drop does not boil nor hiss, but assumes the form of a flattened globule like a globule of mercury. Evaporation occurs very slowly and the drop will remain as such for a long time.

The drop is said to be in the **spheroidal state**, and the reason why evaporation is so slow is that the drop is supported on a cushion of its own vapour through which heat travels with difficulty, too slowly, in fact, to heat the liquid to its boiling point. This vapour is gradually wafted away as it is formed, and so the water gradually evaporates. If the plate is allowed to cool, a time will arrive when the drop comes in contact with the plate and violent ebullition occurs.

*Experiments.* (a) Take a plane metal plate, place it horizontally on a tripod and heat it with a Bunsen flame much above the boiling point of water. Allow a drop of water to fall gently from a pipette on the plate. If the plate is quite flat, it is easy to see between it and the drop; the drop is not in contact with the metal plate. Put one end of a fine wire into the drop (Fig. 109) and connect the other end through an electric bell and a voltaic cell to the plate. When the water is in the spheroidal state the bell is silent. Withdraw the Bunsen flame. When the violent ebullition occurs the bell rings, showing that contact occurs between the water and the plate.

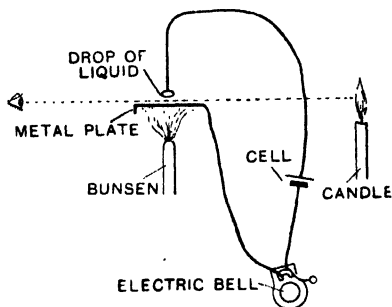


FIG. 109.

(b) Make the end of a poker red-hot and dip it into cold water. For some time no ebullition occurs, the water round the poker being in the spheroidal state. When the poker is sufficiently cooled, violent ebullition occurs. In the same way a hot metal dish may be made to float silently on the surface of water supported on a cushion of vapour.

The use of a heated metallic surface is not essential to the production of the spheroidal state; the only necessary condition is a sufficiently elevated temperature. Thus, if a bath of oil of suitable density is heated to about  $120^{\circ}\text{C}$ ., and water is dropped into it from a pipette, the water forms spheres which do not boil away. If, however, the spheres are touched by a needle, which thereby breaks through the film of vapour, violent ebullition occurs.

Other examples of spheroidal state which may be mentioned are the laundress's mode of testing the temperature of a hot iron, the



licking without injury of a white-hot iron bar, and the fact that the hand, if clean and damp, may be dipped into hot molten lead without injury.

### 9. Sublimation

Under ordinary conditions of pressure some substances do not melt, but pass directly from the solid state to the vapour state, and *vice versa*. Such substances are said to **sublime**; the process is termed **sublimation**. Examples are iodine, arsenic, sulphur, benzoic acid, ice below  $0^{\circ}\text{C}$ ., camphor. By a suitable adjustment of pressure the substance can be made to pass through the liquid state.

*Experiments.* (a) Place some small pieces of iodine in a dry test-tube, and heat it gently. It is easily seen that the iodine does not melt, but passes off into a violet vapour which soon fills the tube. Some of this vapour condenses again on the cooler portions of the tube, forming a thin layer of the solid. The same process takes place more slowly at ordinary temperatures, as may be verified by examining a bottle in which iodine or naphthalene has been kept for some time.



FIG. 110.

(b) Take two watch-glasses of the same size and fitting well round the edges when facing each other. Place a few crystals of benzoic acid in one of them, cover with a filter paper, turn the other upside down over it (Fig. 110), and clip together. Now heat the lower glass gently. The benzoic acid sublimes, passes through the filter paper, and appears as crystals on the upper glass.

(c) Place some roll sulphur in a retort, R (Fig. 111), and lead the stem of the retort into a large flask, F, over which a stream of cold water flows. Heat the sulphur. It will be found that sulphur vapour passes over into the flask and there condenses, forming a yellow cloud of solid particles which collect on the sides of the flask, forming a layer of *flowers of sulphur*.

It is known that ice and snow evaporate at temperatures below the freezing point. Snow often disappears completely by evaporation on very cold days, when no trace of thawing can be detected.

The reverse process to sublimation, *i.e.* the direct change from the vapour state to the solid state, occurs in the formation of *hoar frost* (see page 222).

### 10. Latent Heat of Vaporisation

It has been shown that when water is boiled the temperature of the steam produced is the same as that of the boiling water. On comparing this process with that observed when ice melts, it is evident that the heat given to the water in making it boil has been used in effecting the change of state from liquid to vapour: the heat has been rendered "latent." This heat is given out in the process of condensation of steam to water.

*Experiment.* Place about 250 c.c. of cold water in a beaker, insert a thermometer, and weigh. Boil some water in a flask fitted with a delivery tube, and pass the steam given off into the water in the beaker.

As the bubbles of steam enter the cold water they condense with a crackling sound and the temperature of the water rises rapidly. By weighing the beaker again, the weight of the steam condensed is ascertained.

This experiment does not by itself prove that steam gives out heat in *condens-*

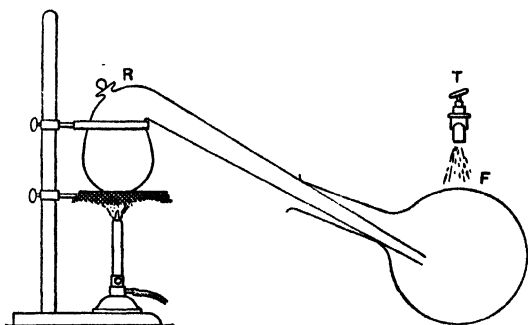


FIG. III.

*ing.* When the steam enters the cold water the following changes take place: (1) It condenses into boiling water without change of temperature; (2) This boiling water mixes with the cold water in the beaker. Hence, if steam gives out heat *in condensing*, the rise of temperature produced by passing the steam into the cold water should be greater than that produced by mixing the same quantity of boiling water with the cold water. Now if this be tried, *i.e.* if the same quantity of water in the same beaker is taken and to it is added a quantity of boiling water equal to that obtained by the condensation of the steam, it will be found that the rise of temperature is much smaller. This shows that the steam in condensing from steam to boiling water without fall of temperature, gives out a considerable quantity of heat.

It is found that a given liquid absorbs, per unit mass, during vaporisation, and evolves, per unit mass, during condensation, a definite quantity of heat which is constant for the same substance under the same conditions. The quantity of heat required to convert unit mass of a substance from the liquid state at the boiling point to the vapour state at the same temperature is called the latent heat of vaporisation of that substance. Thus the latent heat of vaporisation of water at  $100^{\circ}\text{C}$ . is the quantity of heat required to convert unit mass of water at  $100^{\circ}\text{C}$ . into steam at  $100^{\circ}\text{C}$ . It is also the quantity of heat given out by unit mass of steam at  $100^{\circ}\text{C}$ . in condensing to unit mass of water at  $100^{\circ}\text{C}$ . If the gramme is taken as the unit of mass, then the latent heat of vaporisation is expressed in calories per gramme. Hence, if  $L$  denote the latent heat of vaporisation of any substance, then the quantity of heat absorbed during vaporisation, or evolved during condensation, by  $m$  grm. of the substance is  $mL$  calories.

It is to be noted that the latent heat of vaporisation of any substance depends upon the temperature at which vaporisation takes place. If the conditions of vaporisation change the boiling point, it is to be expected that the latent heat of vaporisation will change also.

## 11. Determination of the Latent Heat of Steam

The latent heat of vaporisation of water at  $100^{\circ}\text{C}$ . is usually called the *latent heat of steam*. To determine this quantity, a calorimeter is prepared in the usual way by placing in it a known quantity of water at a known low temperature. A current of *dry* steam from a boiler is then passed either directly into the water, or through a worm immersed in the water, in the calorimeter. The steam condenses, gives out its latent heat, and the temperature of the water rises. When a sufficient rise of temperature is produced, the current of steam is stopped and the temperature of the water in the calorimeter is observed. The calorimeter is then weighed again and the increase of weight gives the mass of the steam condensed.

Denoting the masses of the cold water, calorimeter, and condensed steam by  $m$ ,  $m_1$ ,  $M$  respectively; the initial temperature of the steam and the initial and final temperatures of the water by  $t$ ,  $t_1$ , and  $t_2$ ; the latent heat of vaporisation of water by  $L$ , and the specific heat of the material of the calorimeter by  $s$ ; then, equating the heat given out by the steam in condensing and by its resultant

water in cooling, to the heat absorbed by the calorimeter and its contents,

$$ML + M(t - t_2) = (m + m_1s)(t_2 - t_1);$$

$$\therefore L = \frac{(m + m_1s)(t_2 - t_1)}{M} - (t - t_2).$$

As the experiment lasts only a few seconds, the rise of temperature being very rapid, the cooling correction is not important, but it is well to arrange that the mean temperature of the calorimeter is the same as that of its surroundings. The great difficulty and a source of large error in this method is the difficulty of ensuring that the steam which enters the calorimeter is *dry*. It is obvious that, if the steam carries with it a fine spray of condensed water, the heat evolved in the calorimeter will be much less than if dry steam only entered the calorimeter, and the value of  $L$  obtained will be too low. Various devices for "trapping" or jacketing the current of steam have been adopted for the purpose of *drying* it, *i.e.* removing the fine drops of condensed water in it.

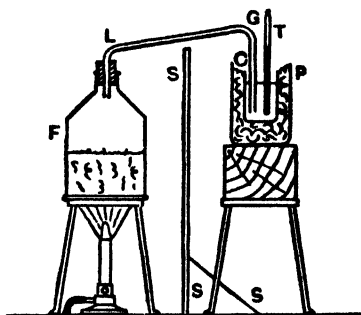


FIG. 112.

*Experiment.* To find the latent heat of steam.—Water is boiled in a copper boiler, F (Fig. 112), and the steam is led by a bent tube, LG, into the calorimeter, C, which is suspended inside a screening vessel, P. SS is a screen which prevents heat passing directly from the boiler to the calorimeter.

Boil the water in F briskly. The boiler should be less than half-full or the steam will carry spray with it. Weigh the calorimeter empty, and again when two-thirds full of water. Stir the water and note the temperature, using a sensitive thermometer. It is advisable to have the initial temperature of the water as much below the air temperature as the final temperature is above it. This obviates any correction for gain of heat from outside sources or loss of heat to them. A preliminary experiment will indicate the best temperature at which to work.

Place the calorimeter in position so that the end of the tube, LG, is well immersed. The issuing steam condenses with a continuous hissing noise. Stir gently. The temperature rises rapidly.



Withdraw the calorimeter when a suitable temperature is reached. Stir well and quickly note the temperature. Weigh the calorimeter again, to determine the mass of steam condensed.

Assume that the temperature of steam is  $100^{\circ}\text{C.}$ , and work out the result as indicated below.

**Example.**—Find the latent heat of vaporisation of water from the following observations. Mass of copper calorimeter = 52.94 gm.; mass of calorimeter and water = 192.14 gm.; mass of calorimeter, water, and condensed steam = 197.12 gm. Temperature of steam =  $100^{\circ}\text{C.}$ ; initial temperature of water =  $14.4^{\circ}\text{C.}$ ; final temperature =  $35.1^{\circ}\text{C.}$

The heat given out (1) by 4.98 gm. of steam at  $100^{\circ}\text{C.}$  condensing to water at  $100^{\circ}\text{C.}$  = 4.98 L calories,

(2) by 4.98 gm. of water cooling from  $100^{\circ}\text{C.}$  to  $35.1^{\circ}\text{C.}$  = 4.98 (100 - 35.1) = 4.98  $\times$  64.9 calories.

The heat absorbed (1) by 139.2 gm. of water in rising from  $14.4^{\circ}\text{C.}$  to  $35.1^{\circ}\text{C.}$  =  $139.2 \times 20.7$  calories,

(2) by 52.94 gm. of copper in rising from  $14.4^{\circ}\text{C.}$  to  $35.1^{\circ}\text{C.}$  =  $52.94 \times 0.095 \times 20.7$  calories.

Equating the heat given out to the heat absorbed,

$$4.98 \text{ L} + 4.98 \times 64.9 = (139.2 + 52.94 \times 0.095) \times 20.7;$$

$$\therefore \text{L} = \frac{144.2 \times 20.7}{4.98} - 64.9 = 535 \text{ calories per gm.}$$

The chief source of error in the experiment described above is that the steam is not dry when it enters the calorimeter; it carries spray with it. A simple method of preventing this is to place a water-trap (Fig. 113) at the delivery end of the steam tube. This trap catches the water which condenses in the tube. It should be provided with a jet, H, and a pinch-cock, R, to allow the condensed water to be drawn off from time to time.

**BERTHELOT'S APPARATUS.**—In order to remove the source of error just

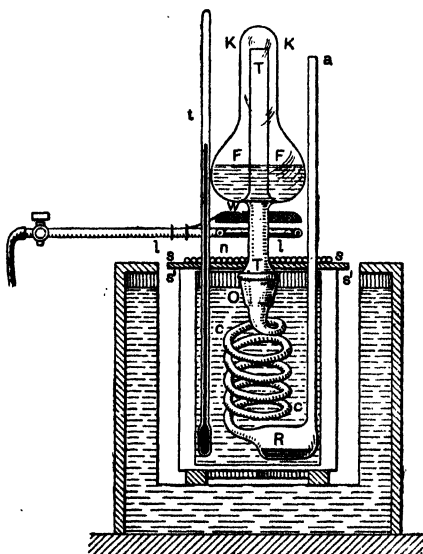


FIG. 114.

mentioned, *Berthelot* devised an apparatus which may be used to determine the latent heat of vaporisation of any liquid. The liquid is boiled in a glass vessel, *K* (Fig. 114), by means of a ring burner, *ll*; the water in the calorimeter is screened from the burner by means of two screens, *ss*, *s's'*, and from other external sources of heat by a copper vessel and a double-walled vessel filled with water. The vapour produced in the vessel, *K*, passes through the short tube, *TT*, into the spiral tube or worm, *cc*, immersed in the water in the calorimeter, and condenses in the reservoir, *R*. The only part of the vapour tube in which condensation is possible outside the calorimeter is the short piece of tube surrounded by the burner. The error arising from partial condensation before the vapour enters the calorimeter is thus reduced to a minimum. The method is quick and is very convenient for the study of the latent heat of vaporisation of organic liquids as the condensed liquid does not mix with the water in the calorimeter. The weight of vapour condensed is given by the increase of weight of the worm. The calculation is similar to that already described.

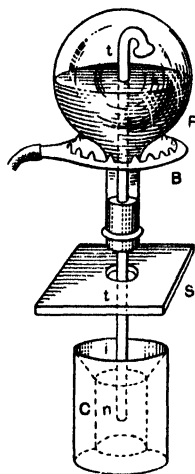


FIG. 115.

*Experiment.* To find the latent heat of vaporisation of water by *Berthelot's method*.—A modification of *Berthelot's apparatus* (Fig. 115) is used. Half fill the flask, *F*, with water, and fit it with a cork and tube, *tt*. Invert and heat by a simple ring burner, *B*. Attach a jet, *n*, to the tube, *t*, by a piece of india-rubber tubing, *i*. The calorimeter, *C*, is supported in an enclosure and shielded from the burner by a screen of wood, *S*. Allow steam to pass from *n* for some time, and then place *C* in position. When the temperature has risen sufficiently, remove *C* and note the maximum temperature. Calculations as before.

By this method *Berthelot* obtained 536.2 for the latent heat of vaporisation of water at  $100^{\circ}\text{C}$ . By a much more elaborate method *Regnault* obtained 536.5. More recent work shows that the latent heat of vaporisation at  $100^{\circ}\text{C}$ . is 540 calories per grm., *i.e.* one gramme of water at  $100^{\circ}\text{C}$ . absorbs 540 calories in becoming steam at  $100^{\circ}\text{C}$ ., or one gramme of steam at  $100^{\circ}\text{C}$ . in condensing to water at  $100^{\circ}\text{C}$ . gives out 540 calories.

The large expansion which occurs when water is turned into steam (Art. 2) accounts in some degree for the large latent heat of vaporisation, for during the change of state the vapour does work against the atmosphere, and, as shown later in Chapter XII., heat and work are mutually convertible.

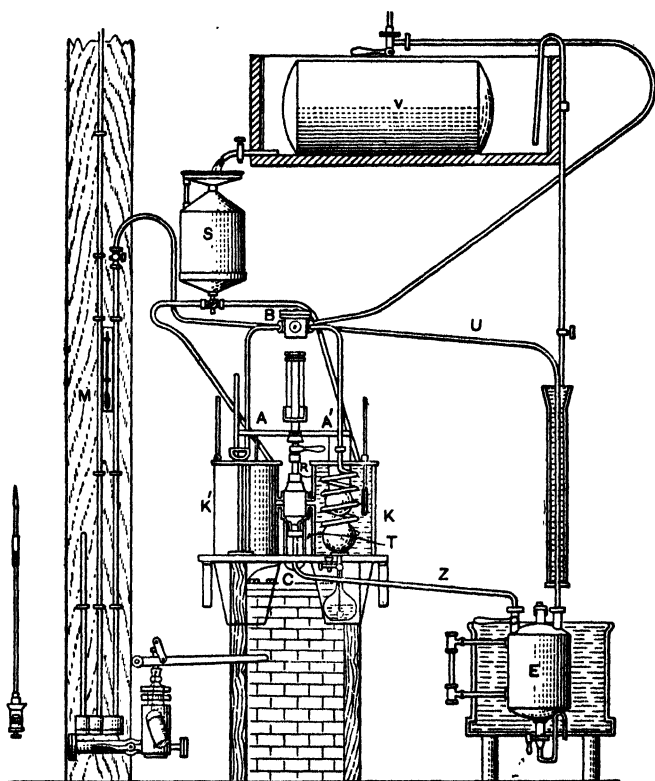


FIG. 116.

## 12. Regnault's Work on the Latent Heat of Steam

*Regnault* carried out a series of careful and elaborate experiments on the latent heat of steam, and found that its value depends upon the temperature at which vaporisation takes place. The real aim of his experiments, however, was to find the **total heat of steam**, i.e. the amount of heat required to raise 1 grm. of water from  $0^{\circ}\text{C}$ .

to  $t^{\circ}\text{C.}$  and to vaporise it at that temperature, the pressure at the time of vaporisation being the maximum pressure of water vapour at  $t^{\circ}\text{C.}$  (see Chapter X.).

The vapour was generated in a large boiler and could be passed into either of two exactly similar calorimeters, K and K' (Fig. 116). Immersed in each calorimeter was a condensing system consisting of two copper spheres and a spiral copper tube, the water resulting being drawn off in a flask and weighed. The two calorimeters were used alternately in an attempt to eliminate corrections for external losses of heat during the experiments.

In order to vary the temperature of the vapour, a large air drum, V, immersed in a water-bath to keep its temperature constant, was connected to the apparatus. By pumping air into, or out of, this drum the pressure in the boiler could be varied at will. The pressure was measured by the manometer, M. By this means the experiments were carried out at pressures varying from  $\frac{1}{8}$  to  $13\frac{1}{2}$  atmospheres.

From the data thus obtained, the results were formulated:— If  $Q_t$  denote the total heat required to raise unit mass of water from  $0^{\circ}\text{C.}$  to  $t^{\circ}\text{C.}$ , and also to convert it into steam at  $t^{\circ}\text{C.}$ , then

$$Q_t = 606.5 + 0.305t.$$

But, since approximately  $t$  units of heat are absorbed by the water in being raised from  $0^{\circ}\text{C.}$  to  $t^{\circ}\text{C.}$ ,

$$Q_t = L_t + t,$$

where  $L_t$  is the latent heat of vaporisation at  $t^{\circ}\text{C.}$  Thus:—

$$L_t = Q_t - t,$$

$$\text{i.e. } L_t = 606.5 + 0.305t - t;$$

$$\therefore L_t = 606.5 - 0.695t.$$

Hence, the total heat required to raise unit mass of water from  $0^{\circ}\text{C.}$  to  $100^{\circ}\text{C.}$ , and to convert it into steam at  $100^{\circ}\text{C.}$  is—

$$Q_{100} = 606.5 + 0.305 \times 100 = 637,$$

$$\text{and } L_{100} = 606.5 - 0.695 \times 100 = 537.$$

These relations for  $Q$  and  $L$  indicate the general result that  $Q$  increases while  $L$  decreases with rise of temperature. The variation of  $L$  with temperature implies also variation with pressure; for, when the latent heat of vaporisation of water at  $t^{\circ}\text{C.}$  is spoken of, it is implied that vaporisation takes place at a pressure equal to the maximum pressure of water vapour at  $t^{\circ}\text{C.}$  (see page 184).



The results of Regnault's work may be illustrated graphically. Assuming that the relation  $L_t = 606.5 - 0.695t$  holds between  $0^\circ \text{C.}$  and  $200^\circ \text{C.}$ , then—

$$\begin{array}{ll} L_0 = 606.5 & Q_0 = 606.5 \\ L_{40} = 578.7 & Q_{40} = 618.7 \\ L_{80} = 550.9 & Q_{80} = 630.9 \end{array}$$

$$\begin{array}{ll} L_{120} = 523.1 & Q_{120} = 643.1 \\ L_{160} = 495.3 & Q_{160} = 655.3 \\ L_{200} = 467.5 & Q_{200} = 667.5 \end{array}$$

From these values the dotted lines shown (Fig. 117) have been plotted. They are straight lines, *i.e.* the changes of  $L$  and  $Q$  with temperature are linear, and from them the latent heat or total heat for any temperature within the range taken can be observed readily.

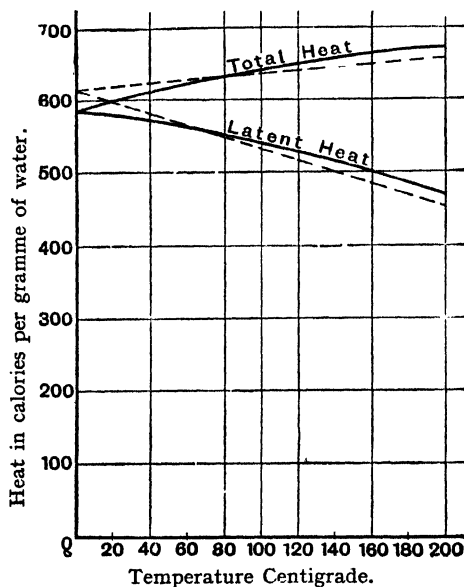


FIG. 117.

Recent work has shown the value of  $L_{100}$  is 540, and not 537 as deduced by Regnault. In calculating  $L$  from  $Q$ , Regnault neglected the variation in the specific heat of water with temperature (page 123). The values of  $L$  and  $Q$  were recalculated by Callendar, and his results are shown by the full curves (Fig. 117). These curves are not straight lines and simple equations connecting  $L$  and  $Q$  with  $t$  cannot be obtained.

### 13. The Steam Calorimeter and Specific Heat Determinations

The latent heat of steam may be applied, just as the latent heat of water is applied in the ice calorimeter, to determine the specific heat of a substance.

The general principle applied in a steam calorimeter is as follows:—If a piece of any substance at a known temperature is suspended in an empty vessel and steam at  $100^\circ \text{C.}$  is passed into the vessel, a mass of steam just sufficient to raise the temperature to  $100^\circ \text{C.}$  will condense on the substance, and this mass will

remain constant so long as the substance remains in the atmosphere of steam. Loss by the dropping of the condensed water from the substance must be guarded against. Hence, if the mass of water which condenses on the substance can be determined, the specific heat of the substance can be calculated.

Thus, if  $m$  is the mass of the substance,  $s$  its specific heat,  $t_1$  its original temperature;  $M$  the mass of the steam condensed,  $t_2$  its temperature, and  $L$  the latent heat at this temperature, then

$$\text{Heat absorbed by the substance} = ms(t_2 - t_1),$$

$$\text{Heat given out by the steam} = ML;$$

$$\therefore ms(t_2 - t_1) = ML,$$

$$\text{i.e. } s = \frac{ML}{m(t_2 - t_1)}.$$

In its simplest form the steam calorimeter consists essentially of a thin metal vessel which can be filled quickly with dry steam from a boiler which communicates with this steam chamber by a wide tube fitted with a suitable stopcock, by means of which the supply of steam may be regulated or stopped at will. A small scale-pan suspended by a thin wire from one arm of a balance hangs freely in this steam chamber. A piece of the substance of which the specific heat is required is placed in this pan and weighed carefully, when the chamber is filled with air only.

The steam is turned on, and, in raising the scale-pan and the substance on it to its own temperature, condenses to water at the same temperature. This water remains on the pan and substance, and, when the final temperature is reached, remains constant in quantity for as long as may be desired. The increase in weight, due to this condensation, can be determined accurately by means of the balance, corrections being made for the buoyancy of *air* in the first weighing, and of *steam* in the last.

**JOLY'S STEAM CALORIMETER.**—The invention and perfection of the steam calorimeter is due to *Joly*. In the form of apparatus first used (Fig. 118), the bent tube marked with arrows is the steam tube leading the steam to the calorimeter from the boiler, which is not shown. The suspension wire from the balance enters the calorimeter through a small hole in the centre of a smooth flat disc which rests on the tubular opening at the top of the calorimeter. The surface of this disc fits accurately to the surface of the edge of the tube on which it rests and so closes the calorimeter; at the

same time it moves freely in a horizontal plane so that the central hole adjusts its position readily to that of the suspension wire. A small quantity of steam escapes between the wire and the edge of

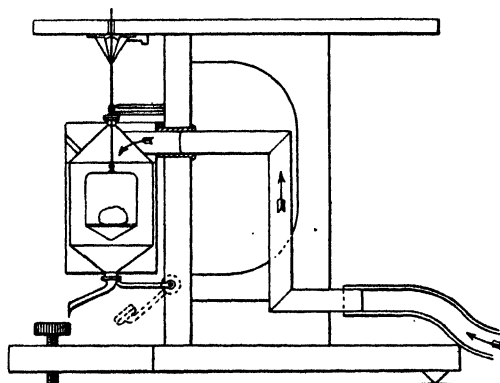


FIG. 118.

the hole in the disc; this is prevented from condensing on the wire by surrounding the wire just above the hole with a spiral of platinum wire which is heated by passing an electric current through it.

The necessary correction for the weight of water condensed by the scale-pan, which is

of platinum, may be obtained by a preliminary experiment with the pan only. If  $w$  denote the water equivalent of the pan, the heat equation given above may be modified to include the scale-pan thus:— $(ms + w)(t_2 - t_1) = ML$ .

With a properly constructed calorimeter the results obtained by this condensation method may attain a high degree of accuracy. One source of error is the possible fall of very small drops of condensed water on the substance and scale-pan carrying it when the steam is first introduced into the cold calorimeter. This error is made almost negligible by admitting the steam suddenly into the chamber, and for this purpose the steam pipe is made wide. After the first sudden admission the supply is regulated so as to provide a gentle current of steam which does not interfere with the process of weighing.

*Experiment.* To find the specific heat of a substance by a steam calorimeter.—A simple steam chamber can be fitted up. It consists of a beaker, B (Fig. 119), fitted with a wooden cover or sheet of cork, C, provided with delivery and exit tubes, I and O, and a small central hole, H, through which a fine platinum wire, V, passes from the balance. The central hole should be covered with a thin aluminium disc, D, as described above. The scale-pan, P, may be of platinum or copper, and should be heavy enough when empty

to keep the wire quite taut. The beaker, B, is placed with a loose cotton-wool packing, W, inside a larger vessel, J.

First, the water equivalent of the pan is found. Take the temperature and pass the steam. After a few minutes the weight of the pan ceases to increase sensibly, and the equilibrium of the balance is maintained very nearly permanent. If the aluminium disc moves freely, it will adjust its position so that the wire always passes freely through the hole in the disc. Care should be taken that water is not condensed on the wire and deposited in the hole. Note the increase of weight, and then shut off the steam. When the beaker is cold, clean and dry the scale-pan, put on a piece of the substance, S, and repeat the experiment. Repeat two or three times until the results are in close agreement.

**Examples.**—(1) Find the water equivalent of the pan of a steam calorimeter from the following data. Initial temperature,  $13^{\circ}\text{C}$ .; temperature of steam,  $101^{\circ}\text{C}$ .; increase of weight of pan,  $0.252\text{ gm}$ .

If  $w$  is the required water equivalent,

$$w \times (101 - 13) = 0.252 \times 540;$$

$$\therefore w = \frac{0.252 \times 540}{88} = 1.55\text{ gm}.$$

(2) Find the specific heat of quartz from the following data. Mass of quartz,  $16.73\text{ gm}$ .; initial temperature,  $15.2^{\circ}\text{C}$ .; temperature of steam,  $100.5^{\circ}\text{C}$ .; increase of weight of pan,  $0.742\text{ gm}$ .

If  $s$  is the required specific heat,

$$(16.73s + 1.55)(100.5 - 15.2) = 0.742 \times 540;$$

$$\therefore 16.73s = \frac{0.742 \times 540}{85.3} - 1.55 = 3.15;$$

$$\therefore s = 0.188.$$

#### 14. The Specific Heat of Gases

Joly devised an improved form of steam calorimeter to determine the specific heat of gases at constant volume. In the improved form, known as the *differential steam calorimeter*, two exactly similar scale-pans hang one from each arm of the balance in a large steam chamber. If the two pans are exactly alike and have the same water equivalent, it is evident that they will counterpoise each other throughout an experiment, and the corrections for buoyancy and water equivalent, and in fact all corrections

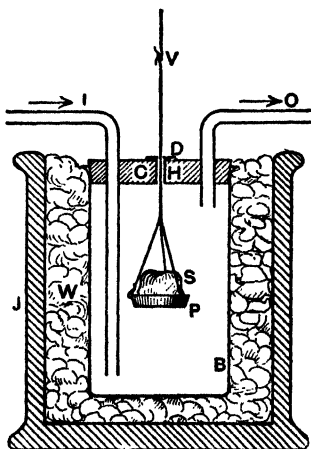


FIG. 119.

necessary for symmetrical sources of error in the calorimeter become unnecessary.

The front and end views of the differential steam calorimeter as used for determining the specific heat of gases at constant volume are shown (Fig. 120). The gas experimented on was placed in two exactly similar spherical shells of copper, made strong enough to stand pressures up to 30 or 40 atmospheres. One shell contained the gas at a pressure of about 20 atmospheres, and in the other

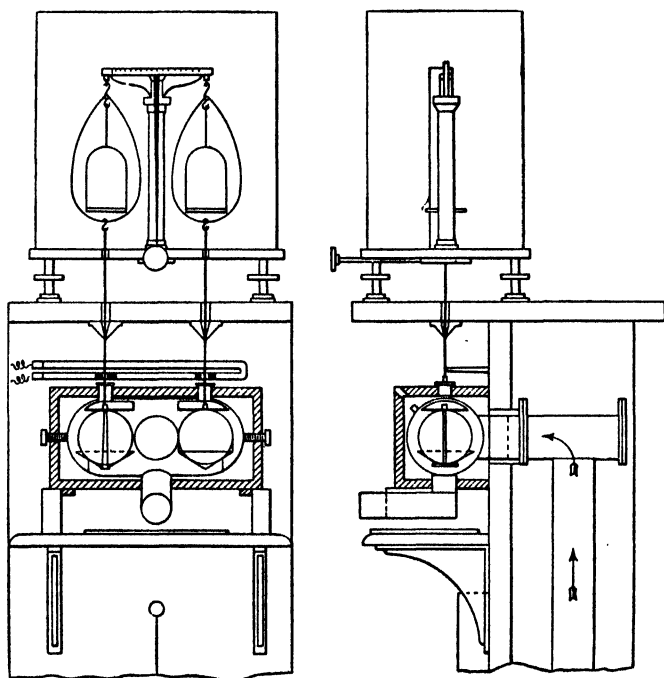


FIG. 120.

the pressure was reduced almost to a vacuum. These shells, with small *catch-waters* attached to them, replaced the platinum scale-pans, and were suspended from the arms of the balance in the steam chamber, and counterpoised carefully at a known temperature. Steam was then admitted in the usual way and a balance obtained again.

It is evident that in these conditions the excess of water which condenses on the shell containing the gas at high pressure is that

which, in condensing to water, gives out the heat required to raise the excess of gas in this shell through the known range of temperature. In this way, the specific heat at constant volume of air and other gases has been determined directly. For very accurate work, corrections have to be made to allow for the changes of volume of the shell due to heating and pressure, but the errors due to these causes are small.

The experiments confirmed the result obtained for air by calculation (page 241). Also, it was shown that the specific heats at constant volume of air and of carbon dioxide increase with pressure. Thus, at about 7 atmospheres pressure the value for carbon dioxide is 0.168, at 22 atmospheres it is 0.174; and for air at 20 atmospheres pressure it is 0.173. The value for hydrogen at atmospheric pressure was found to be about 2.4, and apparently decreases with increase of pressure.

## CHAPTER X

### PROPERTIES OF VAPOURS

**W**HEN water is boiled in an open vessel steam is given off, rises in the surrounding atmosphere and disappears: it is evidently distributed in the surrounding air as an invisible gas. Again, if a bottle containing a volatile liquid such as ether, methylated spirits, or turpentine is simply exposed to the air, the sense of smell indicates that the substance is diffused in a gaseous state in the surrounding air. The process by which substances in the liquid form enter the gaseous state is called, as already explained, *vaporisation*. It takes place at all temperatures, the only effect of temperature being to alter the rate at which the process is carried on. Thus, if a saucer of water is placed in the open air, the water will disappear faster on a dry summer day than on a dry winter day.

#### 1. Vapour Pressure

A liquid, then, gives off vapour from its free surface into the adjacent atmosphere *at all temperatures*. This vapour is gaseous in character and, therefore, may be expected to exert pressure in the same way as a gas does. Hence it is desirable to submit the behaviour of a vapour in this respect to the test of experiment.

*Experiments.* (a) Take a clean and dry barometer tube and set up a simple mercury barometer. Note the height of the mercury column by means of a metre scale, and compare it with that of a standard barometer. Now introduce a *very small* quantity of water into the Torricellian vacuum of the barometer thus made and note the result. This space is not a perfect vacuum, as it contains a very small quantity of mercury vapour derived by evaporation from the liquid mercury. The pressure due to this mercury vapour is, however, negligible at ordinary temperatures. (See Table XIV., page 398.) The water may be introduced from a bent pipette or by passing a small piece of filter-paper soaked in water up the tube into the vacuum.

It will be found that the water vaporises in the vacuum almost instantly, and that the mercury column is depressed slightly.

For example, the height of the column may be reduced from 758 mm. to 752 mm., the pressure of the vapour thus causing a depression of 6 mm. This indicates that the vapour exerts a pressure which is measured by the depression of the mercury column. Thus the pressure of the vapour plus the pressure due to 752 mm. of mercury is equal to a pressure of 758 mm. of mercury, and the pressure of the vapour therefore is equal to that due to 6 mm. of mercury.

Now introduce another *very small* quantity of water into the barometer tube and again note the result. It will be found that again the water vaporises, but not so quickly as before, and the mercury column is depressed again. For example, the height of the column may fall from 752 mm. to 748 mm., thus showing a further depression of 4 mm. This indicates that as the quantity of vapour in the closed space increases the pressure also increases. In this case, the pressure of the vapour increases from 6 mm. to 10 mm. of mercury. Repeat the operation of passing a very small quantity of water into the tube several times, and note the results.

It will be found that the additional quantities of water vaporise more and more slowly, causing in each case a slight but decreasing depression of the mercury column, until finally the water ceases to vaporise and remains as a thin film on the surface of the mercury, and there is no further depression of the mercury column. This shows that the closed space is *saturated* with vapour, and that the pressure of the vapour attains a final value, which is the *maximum vapour pressure under the existing conditions*.

(b) Repeat the experiment, using a barometer tube with a large bulb at the closed end. It will be found that a larger quantity of vapour is necessary to saturate the larger space available, but that the maximum vapour pressure is the same *if the temperature is the same*.

(c) Repeat with alcohol and ether, using a clean barometer tube and clean, dry mercury in each case. It will be found that, at the same temperature, the maximum vapour pressure of alcohol is greater than that of water, and that of ether greater than that of alcohol. For example, at 20° C. the maximum vapour pressure of water is about 17 mm., of alcohol about 60 mm., and of ether about 400 mm. of mercury.

(d) Repeat again with alcohol at two different temperatures, say, in a cold room at 10° C. and a warm room at 20° C. It will be found that the maximum vapour pressure is greater at the higher



temperature, thus indicating that *the maximum vapour pressure of any substance increases with the temperature.*

The above experiments establish the following facts:—A liquid gives off vapour from its free surface at all temperatures, and this vapour behaves like a gas and exerts pressure. Also, when sufficient liquid is present to saturate a closed space with its vapour, the pressure of the vapour attains a maximum value which is constant for a given liquid at a given temperature, but increases as the temperature rises. Further, vapours of different liquids exert different maximum pressures at corresponding temperatures.

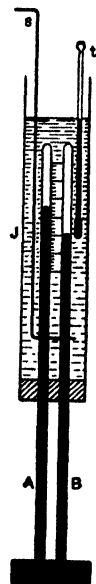


FIG. 121.

## 2. Variation of Maximum Vapour Pressure with Temperature

The result of *Exp. (d)* above indicates that the maximum vapour pressure of a liquid increases with the temperature. It is desirable, therefore, to submit this question of the variation of the maximum vapour pressure with temperature to further experimental investigation.

*Experiments.* (a) Set up two simple barometers, A and B (Fig. 121), and fit them by means of a cork in a wide jacket tube, J. Place a millimetre scale either between the two tubes or behind them so that readings of the mercury columns can be taken to the nearest millimetre. Fill the jacket tube with warm water, about 60° C., and suspend a thermometer, *t*, in the water to indicate the temperature. A stirrer, S, should also be arranged to keep the water in constant motion, and so secure uniformity of temperature throughout. A serves as an ordinary barometer. Introduce into the vacuum of B a sufficient quantity of the liquid, say water, to be vaporised until it exerts its maximum pressure. As the water in the jacket cools, note the depression of the mercury column in B with respect to A, and so determine the maximum vapour pressure of water at a number of different temperatures between 60° C. and the temperature of the room. Then add ice and take readings down to 0° C.

It will be found in studying the results that the maximum vapour pressure increases as the temperature rises, and that for *equal*

increments of temperature the corresponding increments of pressure increase rapidly. As an example the following are the actual results of an experiment with water vapour:—

TEMPERATURE	MAXIMUM VAPOUR PRESSURE IN MM. OF MERCURY
60° C.	160
50° C.	92
40° C.	55
30° C.	31
20° C.	17
10° C.	9
0° C.	5

Here, for equal increments of temperature, each of 10°, between 0° C. and 60° C., the corresponding increments in pressure are 4, 8, 14, 24, 37, 68 mm. of mercury.

No simple law connecting the increase of pressure with the increase of temperature can be obtained. When, however, the results of experiment are plotted, with temperatures as abscissae and pressures as ordinates, a smooth curve (Fig. 122) is obtained. It is possible to obtain from such a graph the maximum vapour pressure at *any* temperature within the range of the graph.

(b) Repeat the preceding experiment, beginning by filling the outer jacket carefully with boiling water. It will be found that the mercury column in B is depressed almost to the level of the mercury in the cistern, and that the column of vapour is so long that great

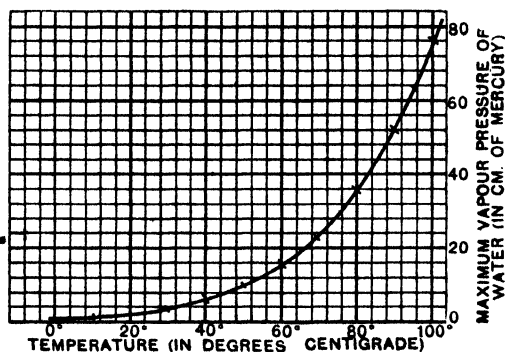


FIG. 122.

difficulty is experienced in maintaining it at a constant temperature. This method of experiment is not suitable therefore under these conditions. A better method is described on page 183.

(c) Repeat the experiment with (i) alcohol, (ii) carbon bisulphide, instead of water, and measure the maximum vapour pressure for temperatures between  $10^{\circ}\text{C.}$  and  $50^{\circ}\text{C.}$  The general results will be found to be similar to those obtained for water vapour, the pressures at  $10^{\circ}\text{C.}$ ,  $20^{\circ}\text{C.}$ ,  $30^{\circ}\text{C.}$ , and  $40^{\circ}\text{C.}$  being 24, 44, 78, and 134 mm. of mercury for alcohol, and 200, 300, 435, and 620 mm. of mercury for carbon bisulphide.

It is thus seen that in all cases the maximum vapour pressure of a liquid increases as the temperature rises, and that *equal* increments of temperature show *increasing* increments of pressure.

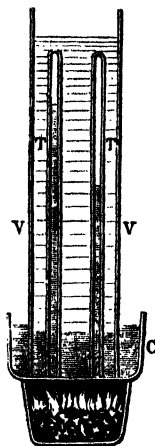


FIG. 123.

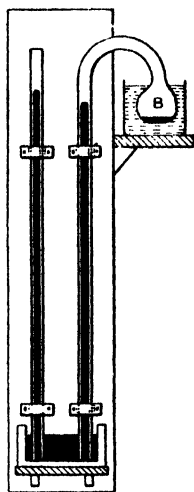


FIG. 124.

### 3. The Work of Dalton, Gay-Lussac, and Regnault

Careful determinations of the maximum pressure of aqueous vapour at different temperatures were made by Dalton, Gay-Lussac, and Regnault.

#### (a) DALTON'S METHOD.—

Dalton's apparatus (Fig. 123) needs little description. C is a cast-iron cistern containing mercury, VV a glass cylinder, and T and T' the barometer tubes. The chief defects of this method were (1) the difficulty of securing a uniform temperature throughout the

water in VV, (2) the difficulty of measuring accurately the difference of level of the mercury columns in T and T' through the cylindrical walls of VV, (3) the limited range of the method. At  $100^{\circ}\text{C.}$  the mercury column in T' is depressed to the level of the mercury in C, and hence observations above  $100^{\circ}\text{C.}$  are impossible.

(b) REGNAULT'S METHODS.—Regnault adopted the general principle of Dalton's method, but the apparatus was modified considerably, and finally three different forms of apparatus for different ranges of temperature were adopted:—

*Apparatus for determinations below  $0^{\circ}\text{C}$ .* It should be noted here that aqueous vapour is given off by ice at all temperatures, the pressure being quite appreciable for a considerable range below  $0^{\circ}\text{C}$ . The bulb, B (Fig. 124), was surrounded by a freezing mixture of calcium chloride and snow. Although that part only of the vapour which is in the bulb, B, is cooled to the temperature of the freezing mixture, the vapour pressure indicated is that which corresponds to this temperature (see Art. 10); for equilibrium can exist only when the pressure throughout the space occupied by the vapour is the same, and, as the pressure in B can never be greater than that corresponding to the temperature of the freezing mixture, it follows that this must be the pressure throughout the space. The temperature of the mixture can be altered by varying the proportions of the constituents. (This form of apparatus was first used by *Gay-Lussac*, and is sometimes referred to under his name.)

*Apparatus for determinations between  $0^{\circ}\text{C}$ . and  $50^{\circ}\text{C}$ .* This apparatus (Fig. 125) is a slightly modified form of Dalton's apparatus already described. Between  $0^{\circ}\text{C}$ . and  $50^{\circ}\text{C}$ . the maximum pressure of aqueous vapour is less than 100 mm. of mercury, hence it is necessary to surround only the upper parts of the barometer tubes with water, as in *Exp. (a)*, Art. 2. This was done by fitting the tubes into a metal box, B, which was closed in front by a sheet of plate-glass through which the measurement of the difference of level of the mercury columns in the two tubes could be made accurately. The temperature of the water in B was varied by means of a spirit lamp adjusted at different distances from the bottom of the box.

*Apparatus for determinations above  $50^{\circ}\text{C}$ .* In this apparatus (see Fig. 104) a principle different from that used in the two determinations above was employed. Regnault applied the fact that, when a liquid boils, the maximum vapour pressure corresponding to the temperature of ebullition is equal to the external pressure. This question is considered fully on page 157, where the apparatus referred to here is described.

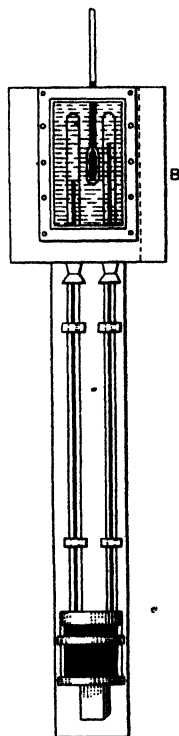


FIG. 125.

*Magnus* and *Dulong* and *Arago* also made careful determinations of the maximum vapour pressure of aqueous vapour at different temperatures, and obtained results almost identical with those of *Regnault*. Later, the values were redetermined by *Holborn* and *Henning* and by *Scheele* and *Heuse*. A summary of the results is given, in a convenient form, in Tables XII. and XIII., pp. 397, 398.

It will be found, on comparing these tables with the figures given on page 181 that the figures bring out the very important result used by *Regnault* in his third set of experiments above. This result may be stated as follows:—*When a liquid boils, the maximum vapour pressure of the liquid corresponding to the temperature of ebullition is equal to the external pressure. Or, the external pressure for each boiling point of a liquid is the same as the maximum vapour pressure for that temperature.*

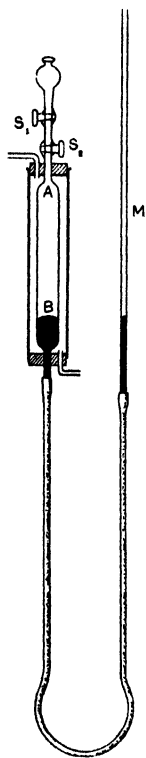


FIG. 126.

#### 4. Dalton's Laws of Vapours

So far the production of a vapour in a vacuum only has been considered, and in the experiments for the determination of maximum vapour pressure the vapour only was present in the closed space. It is necessary now to determine if the results obtained need to be modified when vaporisation takes place in a closed space containing air, or other gas, or vapour with which there is no chemical action.

*Experiments.* (a) The apparatus used is a modification of Boyle's law apparatus (see Fig. 61). A bulb, AB (Fig. 126), is fitted with two stop-cocks,  $S_1$  and  $S_2$ , and is surrounded by a jacket tube. Dry air is first introduced into this bulb and its pressure measured in the usual way by means of the mercury manometer, M. A small quantity of the liquid to be vaporised is then placed in the funnel of the tube and, by opening the stop-cocks,  $S_1$  and  $S_2$ , in turn, a few drops of the liquid may be introduced into the bulb. The increase of pressure due to the vapour may then be determined by arranging the position of the manometer tube, M, so that the air in AB is kept at constant volume. If sufficient liquid is present, the maximum

pressure of the vapour in the presence of air, or other gas, may thus be determined. It will be found to be the same as in a vacuum.

(b) Measure separately (by the method of Art. 1) the maximum vapour pressure of water and of carbon bisulphide at the ordinary temperature and note the values obtained. Then take a piece of barometer tubing, ABC, about 160 cm. long, bend it at the middle to form a U-tube, fill it with mercury and invert into a cistern so as to form a double barometer tube (Fig. 127). Introduce one liquid, say water, into one limb, AB, of the tube and the other liquid, carbon bisulphide into the other limb, CB. The vacuum space will now contain a mixture of the two vapours and the pressure depressing the mercury columns will be the pressure due to this mixture. Measure this pressure and compare with the sum of the individual maximum vapour pressures of the liquids. It will be found that the pressure of the mixture of the two vapours is equal to the sum of the maximum pressures exerted separately by these vapours.

An important difference between the above two experiments should be noted here. In the first experiment, the pressure of the air depends, in accordance with Boyle's law, on the volume it occupies, and in order to get the same *air pressure* before and after introducing the vapour, it is necessary to adjust to the same volume in each case. The pressure of a *saturated* vapour (see Art. 6) at a given temperature is *the same whatever the volume it occupies*, and so no volume adjustment is necessary in the second experiment.

If other experiments similar to those described be carried out, it will always be found that, in the case of a mixture of gases or vapours, or of both, between which there is no chemical action, *the pressure of the mixture is the sum of the individual pressures of the constituents of the mixture*, each constituent exerting, as a part of the mixture, the same pressure that it would exert if it alone occupied the whole space occupied by the mixture. Thus, if a small quantity of ordinary moist air be passed into the "vacuum" space of a barometer tube, the space becomes occupied by a mixture of nitrogen, oxygen, carbon dioxide, water vapour, and

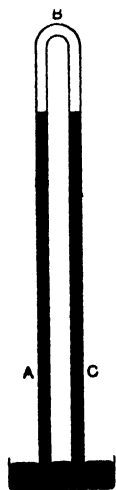


FIG. 127.

mercury vapour. Each constituent of this mixture exerts a definite pressure, which is the same as it would exert if it alone occupied the whole space occupied by the mixture, and the pressure of the mixture is the sum of the pressures that would be exerted by these individual constituents separately. These results have been formulated as laws which are known usually as **Dalton's laws**:—

(1) The maximum pressure exerted by a particular vapour in a closed space at a given temperature depends only on that temperature, and is independent of the presence of other vapours or gases having no chemical action on it.

(2) When several vapours and gases, having no chemical action on one another, are present in the same closed space, the actual pressure exerted by the mixture is the sum of the pressures which would be exerted by quantities of the constituents of the mixture equal to those which are actually present, if separately confined in turn in the same space.

The first of these laws deals with maximum vapour pressure, and is applicable therefore only when the space is saturated with the vapour considered; the second law is applicable whether the space is saturated or not.

In the case of saturated vapours, these laws are true only when the vapours are those of liquids which do not dissolve in or mingle with each other, *e.g.* water and carbon bisulphide. When the liquids mutually dissolve each other, such as water and alcohol, the vapour pressure of the mixture is less than the sum of the vapour pressures which they would exert separately at the same temperature. This could be verified by an experiment exactly similar to *Exp. (b)* above.

Mercury exerts a vapour pressure which although excessively small at ordinary temperatures is quite appreciable at higher temperatures (see Table XIII., page 398). For this reason, in barometer tube experiments at ordinary temperatures, the pressure of the mercury vapour necessarily present can be neglected. Other liquids having very small vapour pressures are some oils, glycerin, sulphuric acid, etc.

### 5. Saturated and Unsaturated Vapours

When a closed space is saturated with vapour, in contact with its liquid, at a given temperature, this vapour exerts its maximum pressure for that temperature, and also is at its maximum density

for that temperature, because the greatest possible quantity of vapour has been introduced into the space. Vapour in this condition is sometimes called **saturated vapour**. When a vapour at a given temperature exerts a pressure less than its maximum pressure for that temperature, it is said to be an **unsaturated vapour**. Vapour in contact with its liquid in a closed space rapidly becomes saturated, for when a steady state is reached, the presence of the liquid is a proof that the limit of vaporisation has been reached.

(I) EFFECT OF PRESSURE AND TEMPERATURE ON SATURATED VAPOURS.—*Saturated vapour* at any temperature exerts the *maximum* pressure corresponding to that temperature, and hence any attempt to *increase its pressure*, such as by compressing it in a closed tube, must fail if any of the liquid be present. The only effect produced by such an attempt would be the condensation of part of the vapour in the space, because, the vapour being already at its maximum density for the given temperature, any attempt at further compression would cause it to pass into the liquid state, while its pressure remains constant. If liquid be not present, and in other exceptional cases, it is possible that the vapour would exert a greater pressure; it is then **supersaturated**. Supersaturation occurs in practice only if foreign matter, *e.g.* dust, is carefully excluded.

On the other hand, if saturated vapour is allowed to expand *in the presence of its liquid*, its pressure remains constant, and the liquid present is gradually converted into vapour, because, directly any small increase of volume takes place, the pressure of the vapour, in accordance with Boyle's law, tends to fall below the maximum pressure corresponding to the conditions of the experiment, and hence vaporisation of the liquid present becomes possible, and thus the pressure is maintained constant. If, however, there is no liquid present, the pressure of the vapour decreases on expansion in approximate agreement with Boyle's law, and the vapour becomes unsaturated.

The effect of change of temperature on a saturated vapour depends also on whether its liquid is present or not. If a liquid and its vapour are heated in a closed space, the liquid is converted into vapour, and the pressure increases at such a rate that, at any given temperature, the vapour present in the space saturates it, and the pressure exerted is the maximum pressure for that temperature. Similarly, if saturated vapour is cooled in a closed space in contact with its liquid, the vapour condenses and the pressure



decreases in such a way that, at any given temperature, the quantity of vapour present in the space is just sufficient to saturate it, and the pressure of the vapour is the maximum pressure for the given temperature.

If, however, saturated vapour is heated in the absence of its liquid, it becomes immediately unsaturated and expands in accordance with Charles's law, or, if the heating takes place at constant volume, its pressure increases in the same way as that of an ordinary gas. On the other hand, if a saturated vapour is cooled in the absence of its liquid, condensation does not always take place at once. The vapour may become supersaturated and then obeys Charles's law.

(2) EFFECT OF PRESSURE AND TEMPERATURE ON UNSATURATED VAPOURS.—*Unsaturated vapours* behave as ordinary gases under change of pressure and temperature—that is, so long as they remain unsaturated, they obey both Boyle's and Charles's laws. According to Regnault, unsaturated water vapour obeys Boyle's law until the pressure reaches almost four-fifths of the maximum vapour pressure. To understand this behaviour, it must be remembered that, for any given vapour, there is for each temperature at which it can exist a definite maximum pressure corresponding to that temperature, and, conversely, for any given pressure to which a vapour is subjected there is a temperature at which this pressure is a maximum.

Hence, if an unsaturated vapour at a given temperature is subjected to increase of pressure, its volume decreases in approximate agreement with Boyle's law, until a pressure is reached which is the maximum pressure for the given temperature, and therefore at this pressure the vapour becomes saturated. Any further increase of pressure produces condensation, as explained above, unless the conditions permit of supersaturation.

Again, if an unsaturated vapour is cooled at constant pressure, its volume will decrease in approximate agreement with Charles's law until a temperature is reached for which the given pressure is a maximum, and at this temperature therefore the vapour becomes saturated, and further cooling produces condensation.

## 6. Ebullition or Boiling

The laws of ebullition or boiling may now be stated formally:—

(1) Ebullition takes place in a liquid at the temperature for which the maximum pressure of the vapour is equal to the external pressure.

(2) The temperature at which ebullition takes place, under a constant pressure, remains constant throughout the process. This temperature is known as the *boiling point* under the given pressure (see page 184).

(3) Under given conditions each liquid has a distinctive boiling point characteristic of the liquid.

In these laws, temperature must be understood to mean the temperature of the *vapour* produced. The temperature of the *liquid* is slightly higher and is found to vary slightly with the nature of the surface of the vessel in which it is boiled.

*Experiment. To show that the maximum vapour pressure of water at the boiling point is equal to the pressure under which boiling is taking place.*—Take a piece of glass tubing about 1 ft. long and about  $\frac{1}{4}$  in. in diameter. Close one end and bend as shown, A (Fig. 128). Fill the tube with mercury to about 1 in. from the open end and the remaining portion with water. Close the tube with the thumb; by inverting the tube, pass the water into the short limb where it rises to the top of the mercury. Remove sufficient mercury from the open limb to bring the level of the mercury in this limb below that in the short limb. Now place the tube, B, in the steam from water boiling in a wide-necked flask. Enough water must be placed in the short limb to saturate the closed space. In a short time, some of the water in the closed limb will be converted into steam, and this steam being saturated will exert the maximum pressure corresponding to the temperature of the surrounding steam. It will then be found that the mercury assumes the same level in both limbs of the tube, thus showing that the maximum vapour pressure of water at the boiling point is equal to the pressure under which boiling takes place. If more than enough water has been introduced into the short limb, allowance must be made for the water remaining on the surface of the mercury.

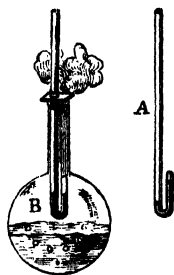


FIG. 128.

## 7. Theory of Ebullition

The process of ebullition, or boiling, can now be dealt with more fully. Consider a bubble of air in a liquid; its walls are formed by the liquid, and from these walls vaporisation goes on until the space

enclosed becomes saturated with the vapour. Let  $V$  denote the initial volume of air in the bubble, and  $P$  the hydrostatic pressure to which it is subjected. The value of  $P$  is determined by the position of the bubble in the liquid; if it is at a depth,  $d$ , below the surface of the liquid, then  $P$  is equal to the atmospheric pressure, *plus* the pressure due to a column of the liquid of height,  $d$ .

As vaporisation goes on into the bubble, the pressure exerted by the vapour increases, until it becomes equal to the maximum vapour pressure, say  $F$ , corresponding to the temperature of the liquid. But, as the total pressure in the bubble must be equal to  $P$  so long as the bubble remains in the same position, the pressure of the air in it must, according to Dalton's second law, be equal to  $(P - F)$ . Hence, if  $V'$  denote the volume of the air after the bubble is saturated with vapour, by Boyle's law

$$VP = V'(P - F) \text{ or } V' = \frac{VP}{(P - F)}.$$

From this it is evident that  $V'$  increases as  $(P - F)$  diminishes, and becomes infinitely great when  $(P - F) = 0$ , *i.e.* when  $F = P$ . This means that when the temperature at any point in the liquid is such that the maximum vapour pressure for that temperature is equal to the hydrostatic pressure at that point, then if a bubble of air, gas, or vapour forms at that point its volume will tend to become infinitely great—that is, it will give rise to an infinite number of bubbles charged with vapour, which rise through the liquid and escape at the surface. This process of formation of vapour in the interior of a liquid, and its final escape at the surface of the liquid, is called *boiling* or *ebullition*.

The pressure due to the surface tension of the walls of the bubble has been neglected. This pressure is given by  $2T/r$ , where  $T$  denotes the surface tension of the liquid-gas surface and  $r$  the radius of the bubble (see *Properties of Matter*, Wagstaff, § 268), and the pressure inside the bubble must be greater than the external pressure by this quantity. When  $r$  is very small,  $2T/r$  is very great, and its magnitude explains why a very high temperature may be necessary to cause the formation of minute vapour bubbles in a perfectly gas-free liquid.

If a liquid is placed in an ordinary glass vessel and heated gradually, the temperature rises and vaporisation goes on freely at the surface of the liquid. Soon, however, small bubbles of air are seen to form on the walls of the vessel, and from them minute

bubbles are given off and rise to the surface; as the temperature rises, this process goes on more rapidly, and bubbles are given off freely from the different points on the walls of the vessel, where air bubbles have been seen to form.

If the heat is applied from below, the upper layers of the liquid will be colder than the lower layers, and it will be seen, at a certain stage of the heating, that bubbles given off from points near the bottom of the vessel are condensed in the upper colder layers before reaching the surface. The condensation of these bubbles of vapour is accompanied by a peculiar noise, familiarly known as *singing*. On further heating, the temperature of the liquid becomes more uniform, and large bubbles of vapour rise rapidly to the surface and escape. The liquid is thus kept in a state of agitation known as *boiling*.

Thus it appears that the commencement of ebullition in a liquid is dependent on the presence of bubbles of air, or other gas, in the liquid or on the walls of the vessel in which it is heated. Experiment shows this to be the case. Provided no bubbles of air form, the liquid may be raised to a temperature considerably above its boiling point without ebullition; but if, in any way, a bubble of vapour or any gas is introduced, boiling takes place at once with explosive violence.

On the other hand, the presence of a very minute quantity of air or other gas in a liquid is sufficient to produce continuous boiling as long as any liquid is left. This can be shown by dropping a small glass bulb containing air and drawn out to a very fine hole into a liquid heated to its boiling point; the air in the bulb will give rise to thousands of vapour bubbles without being diminished appreciably in volume. The same purpose is served also by fragments of charcoal, porous pot, and broken glass used to steady the boiling of liquids in many chemical and physical operations.

Again, the boiling point of a solution of a salt is higher than that of the pure solvent (page 161), as can readily be proved by simple experiment. The boiling point of a solution of a salt is the temperature at which it is in equilibrium with the vapour rising from it. The vapour pressure of a solution is less than that of the pure solvent at the same temperature. Hence, to be in equilibrium with steam at  $100^{\circ}\text{C}$ ., assuming the atmospheric pressure to be normal, the temperature of the solution must be above  $100^{\circ}\text{C}$ .. If the solution is below  $100^{\circ}\text{C}$ ., some of the steam condenses in it and the solution becomes warmer. The steam leaving such a solution is at a temperature greater than  $100^{\circ}\text{C}$ ., but within a

very short distance of the surface it falls to its normal temperature owing to condensation on the walls of the vessel, etc. A thermometer placed in the vapour from a boiling solution indicates therefore the boiling point of the pure solvent; the thermometer must be placed in the solution itself if the boiling point of the solution is required.

### 8. Evaporation

It has been shown that vaporisation takes place at all temperatures in a closed space until that space is saturated with vapour. If, however, the process goes on in the open air it becomes continuous, because it is almost impossible to saturate the atmosphere with vapour. This process of vaporisation in an unlimited atmosphere is called **evaporation**.

Evaporation takes place exclusively at the free surface of the liquid. The vapour formed at the surface penetrates into the adjacent layer of air, and from thence it passes into the next layer, and so on until the vapour is diffused throughout the atmosphere at a uniform rate such that any given layer passes on as much vapour as it receives.

This process is somewhat modified if the air is in motion, for then the layer in contact with the liquid is continually being renewed, and evaporation takes place more rapidly because each layer as it comes in contact with the liquid takes up only a small quantity of vapour, which is carried away at once and thus diffusion is assisted. Moreover, evaporation always takes place into a comparatively "dry" atmosphere, for the successive layers pass on before becoming nearly saturated.

Evaporation is promoted rapidly also if a quick succession of air bubbles be blown through the liquid, for each air bubble exposes a large surface to the liquid and is then swept away immediately.

*Experiments.* (a) Place a small quantity of ether in a watch-glass. In a few minutes the ether will have disappeared by evaporation.

(b) Dip a piece of filter-paper or cloth in water and hang in the open air. In a short time, which depends greatly on the weather, the water will have "dried" out by evaporation.

(c) Place equal quantities of water, alcohol, and ether in similar crystallising dishes and allow to evaporate under the same conditions. The ether evaporates more rapidly than the alcohol, and the alcohol more rapidly than the water.

(d) Place equal quantities of water, or alcohol, in crystallising dishes of different diameters and allow to evaporate under the same conditions. Note the times taken for the liquids to dry up completely. The amount of liquid evaporating per second will be found to be proportional to the diameters of the dishes.

(e) Place equal quantities of ether in two equal crystallising dishes. Direct a gentle current of air over the surface of the ether in one of the dishes. The ether in this dish evaporates much more rapidly than in the other.

(f) Place equal quantities of alcohol in two equal crystallising dishes. Expose one to evaporation in a warm room and the other in a cool room, but otherwise under similar conditions. Evaporation is much more rapid in the former case than in the latter.

From the above experiments it is concluded that different liquids evaporate at different rates. Also, *the conditions favourable to evaporation* can be deduced readily. These conditions are summarised as follows:—

(1) *Dryness of the air.* The less the quantity of vapour present in the air, the more readily does evaporation proceed into it.

(2) *Low atmospheric pressure.* Low pressure facilitates the escape of vapour from the surface of the liquid.

(3) *High temperature, both of the liquid and the air.* The higher the temperature of the liquid the greater the pressure exerted by the escaping vapour, and the higher the temperature of the air the greater the quantity of vapour it will contain before saturation is reached.

(4) *Large extent of free surface of the liquid.* This is evident since evaporation takes place from the free surface.

(5) *Low boiling point of the liquid.* The lower the boiling point the greater the pressure of the vapour at ordinary temperatures.

(6) *Renewal of the air in contact with the surface* of the liquid.

The evaporation of water is a familiar and important process. All the aqueous phenomena of Meteorology have their origin in the evaporation which goes on from the water surfaces of the earth into the atmosphere. Some of these processes will be dealt with in detail in Chapter XI.

### 9. Cold Caused by Evaporation

During evaporation the latent heat necessary to effect the required change of state is absorbed from the liquid itself and its surroundings. This absorption of heat cools the liquid, but as evaporation takes place at all temperatures, the process goes on and a continuous fall of temperature is thus produced. Under favourable conditions this fall of temperature may continue until the freezing point of the liquid is reached and the liquid freezes.

*Experiments.* (a) Place a little ether in a small thin glass beaker, and set it on a wood block with a drop of water between it and the block. Blow a rapid stream of air through the ether. Rapid evaporation is promoted, the ether in turning from liquid to vapour absorbs its latent heat from the glass, wood, and film of water between them, and after a short time so much heat will have been abstracted that the water will freeze. The beaker and block then cannot be separated.

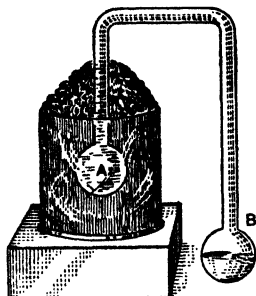


FIG. 129.

(b) *Leslie's experiment.* Place a shallow dish containing a little water and another dish containing strong sulphuric acid under the receiver of an air pump. Exhaust. The water evaporates rapidly, and the vapour formed is absorbed by the sulphuric acid, thus ensuring continuous and rapid evaporation of the water. This process cools the water, and

ultimately a thin layer of ice forms on its surface.

Another instance of the application of the cold produced by evaporation is the method adopted in India for keeping drinking-water cool. The water is placed in porous earthenware vessels through which it percolates slowly; evaporation takes place from the outer surface of the vessel, and the absorption of heat thus produced keeps the water in the desired state of coolness. The same effect may be produced in any vessel by wrapping a wet cloth round it.

A form of apparatus known as the cryophorus was devised by *Wollaston* to illustrate the cooling effect of evaporation. It consists of a bent tube with a bulb at each end (Fig. 129). The apparatus is evacuated of air, and contains only a small quantity of water and water vapour. All the water being passed into the bulb, B,

the bulb, A, is surrounded by a mixture of ice and salt. The cold surface of the freezing mixture condenses the vapour in A as rapidly as it is formed in B, and in a short time the absorption of heat is sufficient to cool the water in B to the freezing point and finally convert it into ice.

Several complicated forms of apparatus have been constructed for freezing water on the principle illustrated by the above experiments; notably Carré's apparatus for freezing by sulphurous acid and by ammonia.

### 10. Vapour Pressure in Communicating Vessels at Different Temperatures

Let A and B (Fig. 130) be two bulbs connected by a tube C. Suppose that A and B both contain some liquid and that the remaining space contains only the vapour of that liquid. Let A and B be placed in baths of temperatures  $t_1$  and  $t_2$ ,  $t_1$  being greater than  $t_2$ , and suppose  $p_1$  and  $p_2$  to be the maximum vapour pressures of the liquid at  $t_1$  and  $t_2$ ,  $p_1$  being greater than  $p_2$ .

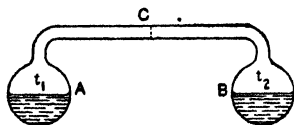


FIG 130.

Suppose a closely fitting piston to be placed in C. Then, since  $p_1$  is greater than  $p_2$ , the piston will be forced towards B. As it moves towards B it tends to increase the pressure in B, but, since the pressure cannot rise above  $p_2$ , some of the vapour in B will be condensed. Similarly its motion away from A causes some of the liquid in A to evaporate. This action proceeds whether the piston is present or not, and so it is seen that the effect of A and B being at different temperatures is that there will be a continual transference of vapour from A to B until all the liquid in A has evaporated and the pressure throughout the vessel is  $p_2$ , the maximum vapour pressure corresponding to the lower temperature  $t_2$ . This explains the principle of Regnault's method of determining the maximum vapour pressure of water below  $0^\circ\text{C}$ ., the action of Wollaston's cryophorus, and the possibility of distillation.

Next, suppose that A contains pure water and B contains a solution of a salt, say calcium chloride, in water, the whole apparatus and its contents being initially at  $100^\circ\text{C}$ . Then, since the vapour pressure in B is less than the vapour pressure in A, distillation will occur from A to B. Heat will be used up in A in this process and



heat will be given to B. Hence the temperature of the pure water will fall and that of the solution will rise. This process will continue until the temperature of the solution is so much above that of the pure water that its vapour pressure is equal to that of the water, when equilibrium occurs. (See page 161.)

## 11. Vapour and Gas

An unsaturated vapour at temperatures considerably higher than the boiling point of the liquid from which it is derived is usually called a gas. The technical difference between a vapour and a gas turns upon the following point:—If an unsaturated vapour is below a certain temperature, known as the *critical temperature* (see page 254) for the substance, it can always be condensed or liquefied by increasing the pressure until the maximum vapour pressure for the temperature is reached. If, however, the vapour be above the critical temperature, it cannot be condensed by increase of pressure however great, and is properly called a *gas*. Hence a gaseous substance at temperatures below its critical temperature is properly called a *vapour*, but above the critical temperature it should be called a *gas*. The critical temperature for carbon dioxide is  $30.9^{\circ}\text{C.}$ ; hence, above this temperature carbon dioxide is a gas, but below this temperature, if apparently gaseous, it is the vapour of liquid carbon dioxide.

## 12. Liquefaction of Gases

Experimental evidence shows that the properties of gases are continuous with those of unsaturated vapours at temperatures considerably above the boiling points of their liquids. Hence, if it is wished to condense any given gas, the method of doing so is indicated by the results, in the two cases referred to above, in connection with unsaturated vapours (Art. 6). All gases and vapours may be liquefied by the combined application of pressure and cold, and, in many cases, the application of either pressure or cold separately produces the desired effect. As a simple example, suppose it is desired to liquefy unsaturated water vapour, which exists at a temperature of  $200^{\circ}\text{C.}$  and under the normal atmospheric pressure. Three courses are open:—

(1) *Application of pressure at constant temperature.* It is known that condensation sets in at any temperature as soon as the maximum vapour pressure for that temperature is reached. Hence, in this case, water would begin to form when the pressure applied became

equal to that due to 11647 mm. of mercury (see Table XIII., page 398).

(2) *Application of cold at constant pressure.* In this case condensation would take place as soon as a temperature is reached, for which the existing pressure is the maximum vapour pressure—that is, water would be formed when the vapour is cooled to  $100^{\circ}\text{C}$ .

(3) *Combination of (1) and (2).* In this way condensation might be produced by cooling the vapour to, say,  $150^{\circ}\text{C}$ ., and increasing the pressure to 3568.7 mm. of mercury (see Table XIII., page 398).

The method adopted in any particular case depends on circumstances; it is very much easier to apply pressure than to cool a gas down to a very low temperature, but a gas is distinguished from a vapour by the property that it cannot be liquefied by pressure alone as it is above its critical temperature (Art. 11). Hence, unless a gas is first cooled, *at least below its critical temperature*, it is impossible to liquefy it by the application of pressure alone. This explains why oxygen, nitrogen, air, hydrogen, etc., so long withstood all attempts at liquefaction; the critical temperatures of these gases are so very low, that it is only in comparatively recent years that experimenters have been able to cool them below their critical temperatures, and thus effect their liquefaction at very high pressures. Practical methods of liquefying gases are described in Chapter XIV.

### 13. Vapour Pressure Thermometers

As pointed out in Arts. 1, 2, the maximum vapour pressure of a liquid depends only on the temperature of the liquid. If the maximum vapour pressure of a liquid at all temperatures has been determined and tabulated once for all, then, as *Kelvin* pointed out, the process may be reversed and a vapour pressure determination may be used to find the temperature. This method is free from several of the troublesome errors which complicate mercurial thermometry.

A form of vapour pressure thermometer for moderate temperatures is shown (Fig. 131). The lower half of the bulb, B, and a part of the tube, CDF, is occupied by mercury. There is a small quantity of ether above the mercury in B, all the air having been removed by boiling the ether for some time before sealing the top

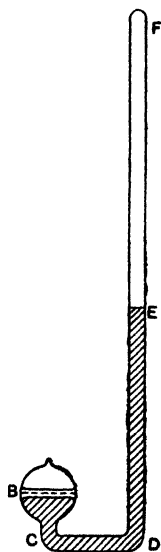


FIG. 131.

of the bulb. There is a vacuum above the mercury in DF. The difference in the levels of the mercury in B and in DF is a measure of the vapour pressure of ether at the given temperature. The difficulty in this form of thermometer is to apply the proper correction for temperature, and therefore density, of the balancing of mercury in DF.

#### 14. Vapour Density

Avogadro's hypothesis states that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. Since the molecular weight of hydrogen is 2, it follows that under the same conditions of temperature and pressure

$$\frac{\text{Density of a gas}}{\text{Density of hydrogen}} = \frac{\text{Molecular weight of the gas}}{2},$$

and the most direct method of determining the molecular weight of a gas is to find its density relative to hydrogen. In Chemistry, therefore, vapour density plays a more important part than vapour pressure.

If the substance is a *gas under ordinary conditions* its relative density may be found by the simple process of taking a large glass vessel provided with a stopcock and weighing it (a) when evacuated, (b) when full of gas at known temperature and pressure, (c) when full of hydrogen at known temperature and pressure. Let these three weights be  $w_1, w_2, w_3$  grammes respectively. Then, if for simplicity it is assumed that the temperature and pressure are the same in the two cases,

$$\frac{\text{Density of the gas}}{\text{Density of hydrogen}} = \frac{w_2 - w_1}{w_3 - w_1}.$$

The density of hydrogen at  $0^\circ\text{C}$ . and 760 mm. pressure is, however, a well-known physical constant— $0.00009$  grammes per c.c.—which has been determined once for all. The third weighing, therefore, may be dispensed with if, in its place, the volume of the vessel is found, and this is done easily by filling it with cold water and weighing. Let the weight filled with water be  $w_4$  grammes. Then,

$$\text{Volume of vessel} = (w_4 - w_1) \text{ c.c.}$$

Weight of hydrogen which would fill the vessel at  $0^\circ\text{C}$ . and 760 mm.

$$= (w_4 - w_1) \times 0.00009 \text{ grammes.}$$

Now, if  $t^{\circ}\text{C.}$  and  $p$  mm. are the temperature and pressure when the vessel is filled with the gas, then

Weight of gas which would fill the vessel at  $0^{\circ}\text{C.}$  and 760 mm.

$$= (w_2 - w_1) \times \frac{273 + t}{273} \times \frac{760}{p};$$

$$\therefore \frac{\text{Density of the gas}}{\text{Density of hydrogen}} = \frac{(w_2 - w_1) \times \frac{273 + t}{273} \times \frac{760}{p}}{(w_4 - w_1) \times 0.00009}$$

If the substance is a *liquid at ordinary temperatures and pressures*, it must be vaporised by heat. Then, from the volume, mass, pressure, and temperature of a quantity of the vapour formed the density may be found.

### 15. Determination of Vapour Density

The chief practical methods employed in the determination of vapour densities are those of *Gay-Lussac* (or *Hofmann*), *Dumas*, and *Victor Meyer*.

(1) **GAY-LUSSAC'S (OR HOFMANN'S) METHOD.**—In this method a known weight of liquid is introduced into the space above the mercury in a barometer tube. The tube is then heated to a known temperature. The liquid evaporates, and its volume and pressure can be measured. The density can then be found as described above.

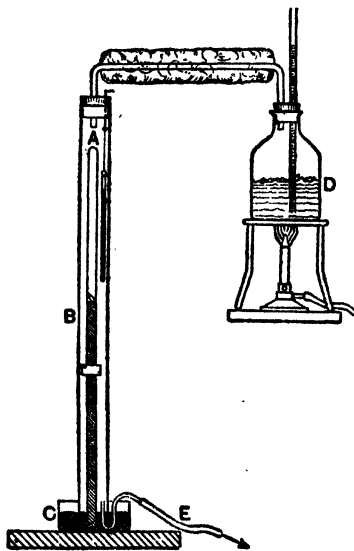


FIG. 132.

**Experiment.** Find the molecular weight of carbon tetrachloride.—Set up the apparatus as shown (Fig. 132). A is a barometer tube about 1.5 cm. in diameter, B a wider tube used as a jacket, C a reservoir of mercury, D a boiler to supply steam to B, and E an exit tube for the steam from B. Clean the tube, A, fill it with clean, dry mercury, and invert it in the reservoir of mercury, thus forming a barometer. This barometer should be good enough to

read to within 1 mm. of a standard barometer. Measure the height  $H$ , of the mercury with a vertical metre scale, or, better, by a mm. scale etched on a long piece of plate-glass mirror placed behind A. If a scale on a thick plate-glass mirror is used, all errors of parallax are avoided. Take the temperature of the mercury, and then calculate the height of the barometer at  $0^\circ \text{C}$ .

Now take a small glass stoppered bottle, about 1.5 cm. long, weigh it, partly fill it with carbon tetrachloride, and weigh again. The difference gives the weight of liquid taken,  $w$  grm. Push the bottle under the end of A. It rises quickly to the top of the mercury. Now pass steam through the jacket from D. A thermometer suspended in B gives the temperature. As the inner tube gets hot the carbon tetrachloride vaporises, and the mercury column falls.

When the descent has ceased, note the temperature,  $t^\circ \text{C}$ ., and read on the scale (i) the height of the top of the tube A, (ii) the height of the mercury column in A, and (iii) the level of the mercury in the reservoir. The difference between (i) and (ii) gives the length of the tube occupied by the vapour. The difference between (ii) and (iii) multiplied by the factor  $(1 - 0.000182t)$  gives the height of the mercury column corrected for temperature, and this corrected height subtracted from the barometric height gives the pressure,  $p$  mm., of the vapour.

The steam is now turned off, and the tube A is taken out and cleaned. Fill the part of A previously occupied by the vapour with water (or mercury), weigh the water (or mercury) and so determine the volume,  $v$  c.c., of the vapour.

Thus, the volume,  $v$  c.c., occupied by  $w$  grm. of carbon tetrachloride at  $t^\circ \text{C}$ . and a pressure of  $p$  mm. of mercury is found. Hence, the molecular weight of carbon tetrachloride is

$$2 \times \frac{w}{v} \times \frac{273 + t}{273} \times \frac{760}{p} \times \frac{1}{0.00009}.$$

In this description no allowance has been made for the expansion of the glass of the tube A, or of the scale. The corrections are negligible.

**Example.**—Calculate the molecular weight of carbon tetrachloride from the following observations. Observed height of barometer at  $19^\circ \text{C}$ ., 773.5 mm. Weight of carbon tetrachloride, 0.1066 grm. Temperature of steam jacket,  $101^\circ \text{C}$ . Height of mercury column at  $101^\circ \text{C}$ ., 481.5 mm. Volume occupied by the vapour, 54.30 c.c.

Using the notation above,

$$p = 773.5 (1 - 0.000182 \times 19) - 481.5 (1 - 0.000182 \times 101) = 298.2 \text{ mm.}$$

$$v = 54.30 \text{ c.c. } w = 0.1066 \text{ grm. } t = 101^\circ \text{C}.;$$

∴ Molecular weight of carbon tetrachloride

$$= ? \times \frac{0.1066}{54.30} \times \frac{273 + 101}{273} \times \frac{760}{298.2} \times \frac{1}{0.00009} = 153.$$

The formula of carbon tetrachloride is  $\text{CCl}_4$ . The atomic weight of carbon is 12, the atomic weight of chlorine is 35.4, whence the molecular weight of  $\text{CCl}_4$  is  $12 + 4 \times 35.4 = 153.6$ .

(2) DUMAS' METHOD.—In this method a quantity of liquid is introduced into a glass bulb. The bulb is then heated to a known temperature, so that the bulb is filled completely with the vapour. The weight and volume of the vapour are then found, and the vapour density can then be calculated.

*Experiment. Find the vapour density of chloroform.*—A light glass bulb of about 200 c.c. capacity is drawn out to a fine point (Fig. 133). It is weighed; this gives the weight,  $w$  grm., of the bulb filled with air at the observed temperature and pressure. By warming the bulb gently, and then placing the orifice beneath the surface of the liquid whose vapour density is to be determined and allowing the bulb to cool, a quantity of the liquid is introduced. This should be in considerable excess of that required to fill the whole bulb with vapour, as it is necessary to ensure the air being expelled from the bulb in the process of vaporisation; usually about 10 c.c. will suffice.

The bulb is now placed in a bath of liquid heated to a constant temperature, which should be about  $20^\circ \text{C}$ . above the boiling point of the liquid under examination. When the whole of the liquid in the bulb has been transformed into vapour the orifice of the bulb is sealed by a blowpipe flame. Thus the bulb is filled completely with the vapour at the temperature of the bath and the pressure of the atmosphere. After cooling, the bulb is weighed,  $w_1$  grm.

The end of the sealed tube is then broken off under water; the water enters and fills the bulb. The bulb is now weighed again, together with the piece of glass broken off. This gives the weight,  $w_2$  grm., of the bulb filled with water. Then, the volume of the bulb is  $(w_2 - w)$  c.c. This is not quite exact, but the error is negligible compared with the errors of experiment and with the deviations from the gas laws of vapours at temperatures not far above their condensation temperatures.

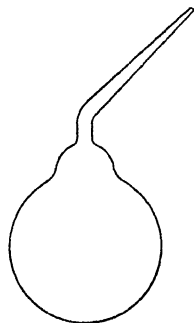


FIG. 133.

Let  $t^{\circ}$  C. be the temperature and  $p$  mm. of mercury the pressure at the time of the first weighing. The weight of the air filling the bulb at this temperature and pressure is—

$$(w_2 - w) \times 0.001293 \times \frac{273}{273 + t} \times \frac{p}{760} \text{ grm.} = x \text{ grm.}$$

Then, the weight of the bulb if evacuated is  $(w - x)$  grm., and the weight of vapour contained in the bulb at the second weighing is

$$\begin{aligned} w_1 - (w - x) \\ = w_1 - w + x \text{ grm.} \end{aligned}$$

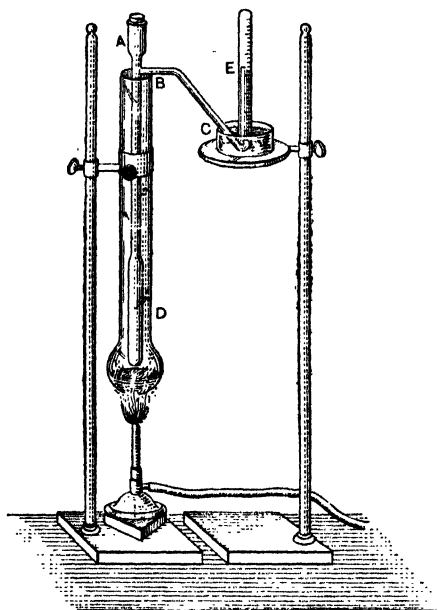


FIG. 134.

Several corrections have been omitted in the above, but a high order of accuracy is not possible and, indeed, is unnecessary, since the true purpose is to decide only whether the molecular weight is  $M$ , say, or some multiple of  $M$ .

The method as described above can be used only at temperatures below that at which glass softens (about  $400^{\circ}$  C.). *Deville and Troost* and others have substituted porcelain and metal for glass, and thus made the method applicable up to very high temperatures, using baths of the vapour of such substances as sulphur, zinc, etc.

(3) VICTOR MEYER'S METHOD.—This method also possesses the advantage of being applicable over a considerable range of temperature; it is also easy to manipulate, and the determination can be made with a small quantity of the substance. In the method a known weight of the liquid is introduced into a large vessel, which can be heated in a suitable bath. The liquid is heated so that it vaporises and a volume of air equivalent to the volume of the vapour produced is displaced and collected in a graduated vessel.

*Experiment. Find the vapour density of ether.*—The apparatus (Fig. 134) consists of a rather wide glass tube, A, narrowed in the upper part and then widened again near the top so as to admit an india-rubber stopper, the length of the tube being about 60 cm. Near the top of the narrow tube is a side tube, BC, bent as shown. Surrounding A is a wider tube, D, containing a quantity of water, naphthalene, or other substance suitable for heating the glass bulb, according to the temperature required to vaporise the liquid, the bulb being so placed as to leave a clear space all round it.

A graduated cylinder, E, is filled with water, inverted, and made ready for placing over the end of the side tube, BC. The stopper being inserted, the jacket is heated, and the temperature of the glass tube, A, raised to that of the bath. Owing to the expansion of the air bubbles pass out through the side tube, BC.

When the temperature becomes constant the bubbles cease, E is placed over the end of BC, the stopper is withdrawn from A, a weighed amount, about 0.2 gm., of the substance in a small bottle or bulb is dropped in and the stopper replaced immediately. A little sand, glass wool, or asbestos should be put in the bottom of the tube to prevent breakage when the bulb is dropped in; also a device may be used by which the substance may be dropped into the tube without removing the stopper.

If the experiment is successful, the substance will be vaporised rapidly, and an equivalent volume,  $v$  c.c., of air will be expelled through the side tube. This is measured carefully and the temperature,  $t^{\circ}\text{C.}$ , and pressure,  $p$  mm., of the room noted. If  $h$  mm. is the height of the water surface in E above that of the water in the vessel in which it stands, and  $f$  mm. is the maximum vapour pressure of water at  $t^{\circ}\text{C.}$ , then the volume that the air in E would have at  $0^{\circ}\text{C.}$  and 760 mm. is given by

$$V = v \times \frac{273}{273 + t} \times \frac{p - \frac{h}{13.6} - f}{760}.$$



If  $w$  grm. is the weight of liquid placed in the bottle, then the density,  $D$ , of the vapour compared with hydrogen under the same conditions is given by

$$D = \frac{w}{0.00009 \times V}$$

Provided only that the temperature of the jacket is constant and sufficiently high to ensure rapid vaporisation of the liquid, the actual temperature employed need not be known. This will be clear if it be remembered that the volume of the air which is actually displaced and collected in the graduated tube is at the temperature of the room; the vapour of the substance occupies precisely the same volume which this air would have occupied at the temperature of vaporisation. Therefore the volume which the vapour would occupy if it could be collected as a vapour at the temperature of the room is obtained.

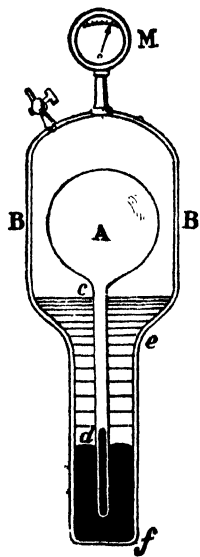


FIG. 135.

**Example.**—A small bottle containing 0.054 grm. of ether was dropped into the tube of a Victor Meyer apparatus. The air expelled occupied 18 c.c. at  $21^{\circ}\text{C}$ ., the barometric height being 765 mm. and the height of water in the collecting tube being 140 mm. above the level of the water in the trough. Find the molecular weight of ether vapour.

From Regnault's tables (Table XIII., page 398),  $f = 18.5$  mm. Hence—

$$V = 18 \times \frac{273}{294} \times \frac{765 - \frac{140}{13.6} - 18.5}{760} = 16.2 \text{ c.c.};$$

$$\therefore D = \frac{0.054}{0.00009 \times 16.2} = 37.$$

Hence, the molecular weight of ether = 74.  
Confirm this from the formula  $(\text{C}_2\text{H}_5)_2\text{O}$ .

## 16. Vapour Densities of Saturated Vapours

It is a more difficult task to determine the density of a saturated vapour than the density of an unsaturated vapour. In order to determine the volume of unit mass of saturated steam at any temperature, *Fairbairn and Tate* used the apparatus shown diagrammatically (Fig. 135). The bulb, A, contains a known weight of water, and the outer vessel, B, contains sufficient water to secure saturation at all temperatures. The vessels contain no air, only water and water vapour, and the mercury which separates the water and vapour in A from that in B. The gauge, M indicates,

the pressure in B, and it is evident that so long as the pressure in A is equal to that in B the level of the mercury inside and outside the tube, *cd*, will not change.

In an experiment, the whole apparatus is raised in temperature until the mercury in *cd* begins to rise. It is then known that at this temperature the mass of water in A is just sufficient to fill the volume of A as saturated steam at that temperature. The volume of A can be determined by calibration with mercury, and hence the volume of unit mass of the saturated steam or, if required, the density of saturated steam at the observed temperature may be determined.

## CHAPTER XI

### HYGROMETRY

**E**VAPORATION is going on constantly from the surface of the sea, rivers, and lakes. Therefore there must always be some water vapour in the air. This water vapour when quite free from small particles of condensed water is invisible, but its presence may be proved by one or two simple experiments.

Thus Fig. 136 depicts a flask fitted with a delivery tube and containing water. On boiling the water a steady current of water vapour issues from the delivery tube and mixes with the air in the

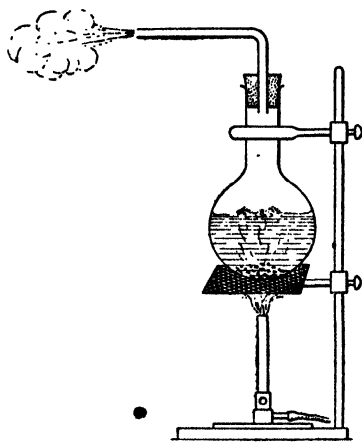


FIG. 136.

room. Water vapour must therefore be diffused throughout the air in the room, although, with the exception of the small cloud of condensed vapour at the mouth of the tube, there is no visible sign of its presence. Note that (a) the *dry* water vapour in the flask and in the tube is invisible, (b) the jet of steam issuing from the tube is invisible until it is condensed by contact with the colder air to form the small cloud which appears *at a short distance* from the mouth of the tube, (c) the cloud consists of minute drops of water, (d) the water drops of the cloud evaporate quickly and the vapour

diffuses throughout the air in the room.

Again if a glass vessel be filled with cold water, the outside thoroughly dried, and the vessel be brought into a "living room," beads of moisture, resulting from the condensation of the vapour in the air, will form quickly on the surface of the cold glass.

#### 1. Relative Humidity

The air is said to be *dry* or *moist* according as it contains little or much moisture, but the condition of the air, in relation to dryness

or moisture, involves two factors: (1) the quantity of water vapour *actually present* in the air, (2) the quantity of water vapour necessary to *saturate* the air under the same conditions. It is on the *ratio* of these two factors that the sensations of dryness or moisture depend chiefly, and not on the first alone. Thus, the air in a warm room may contain actually more aqueous vapour than the outside air and yet be *drier* because the amount required to saturate it is so much greater; for it has been shown that the mass of vapour required to saturate a given space increases with the temperature, and is independent of the presence of air or other gas in that space. The hygrometric state of the air, considered as the ratio of the mass of aqueous vapour actually present in a given volume to the mass of vapour required to saturate the same volume, at the same temperature, is called the *humidity*, or *relative humidity* of the air: *i.e.*

$$\text{R.H.} = \frac{\text{Mass of vapour present in the given volume of air}}{\text{Mass of vapour required to saturate the same vol. at the same temp.}}$$

The relative humidity is expressed usually *either* as a ratio *or* as a percentage.

**Example.**—If a cubic metre of air at a particular temperature contains 10 gm. of aqueous vapour, and if 30 gm. are required to saturate it at the same temperature, the relative humidity is  $\frac{10}{30} = \frac{1}{3}$ , or 33·3 per cent.

## 2. Determination of Relative Humidity by the Absorption Method

If by actual experiment the mass of water vapour really present in a given volume of air can be found, and also the mass of vapour required to saturate the same volume at the same temperature can be calculated, the relative humidity of the air can be determined at once.

For this purpose a quantity of the air is drawn through a series of drying tubes containing fragments of pumice-stone soaked in concentrated sulphuric acid. To effect this, the drying tubes are connected together by short communicating tubes, and one end of the series is connected to the upper tube of an aspirator, while the other opens into the outer air (Fig. 137). The aspirator is a large vessel of from 5 to 10 litres capacity, having a tube fitted with a stopcock at its upper and lower ends. The aspirator is filled with water, and, when communication with the drying tubes is effected, the upper and lower stopcocks are opened. The water then flows out by the lower tube, and air is sucked in through the drying tubes and is collected in the upper part of the aspirator.

The air, in passing through the drying tubes, is deprived of its moisture, and, by determining the increase in weight of the first two or three tubes, the weight of moisture deposited is obtained. The volume of the air drawn through the apparatus is determined by the weight of water which has escaped from the aspirator. If great accuracy is required, this volume must be corrected for the temperature of the water in the aspirator and the aqueous vapour present (see Art. 6). This volume being determined, it remains only to calculate from Regnault's table (Table XVI., page 399) the

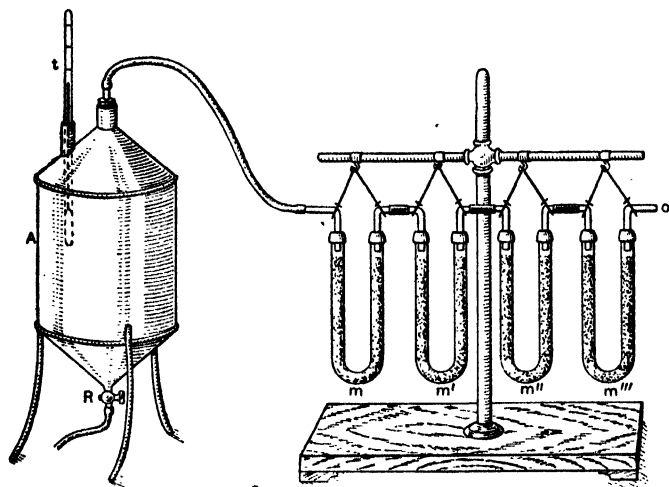


FIG. 137.

mass of water vapour necessary to saturate it at its initial temperature. Then the relative humidity is deduced from the ratio—

$$\frac{\text{Quantity of vapour actually present in the given volume.}}{\text{Quantity of vapour that would saturate this volume at the existent temp.}}$$

*Experiments.* (a) Set up the apparatus and perform the experiment as described above. Consult Regnault's table and deduce the relative humidity.

(b) Instead of consulting Regnault's table, a direct determination may be made of the quantity of water required to saturate a given volume of air. Attach to the inlet of the drying tubes a long glass tube of  $1\frac{1}{2}$  in. bore containing crushed pumice-stone moistened with

water. The air is now saturated by the time it reaches the drying tubes. To remove any drops of water carried mechanically by the stream of air insert a tube packed with cotton-wool between the saturating tube and the drying tubes. The drying tubes thus record the mass of vapour required to saturate air at its temperature when leaving the long tube. To measure the temperature insert a thermometer in the long tube, with its bulb near the connection to the drying tubes. Since the temperatures of the air in the two experiments are not likely to be the same a small temperature correction is necessary.

The two preceding experiments can be combined in one experiment by putting all the tubes in series. The air must pass first through the tubes of *Exp. (a)*, and then through the saturator and tubes of *Exp. (b)*. In this case the volume of air passing through the tubes need not be measured, and the suction of air can be arranged conveniently by joining the tubes to a water-pump working gently. The tubes can then be left for any suitable period of time.

### 3. Dew-Point

Under ordinary circumstances the quantity of water vapour present in the air is not sufficient to produce saturation, and the pressure due to the vapour present is therefore less than the maximum vapour pressure for the temperature of the air. If, however, the air be cooled gradually a temperature is reached at which the amount of vapour actually present is sufficient to produce saturation. This temperature is called the **dew-point**. At the dew-point the air is saturated with the vapour actually present, and the pressure due to the vapour is therefore the maximum vapour pressure at the dew-point.

When the air is cooled below the dew-point condensation *begins* at the dew-point, and as the temperature falls the excess of vapour over the amount necessary to give saturation at any temperature condenses out. If the air is cooled by contact with the surface of a cold body, the layer of air in contact with the surface quickly reaches the dew-point and a film of condensed moisture or dew is deposited on the cooling surface. If, however, the air is cooled, as a whole or in part, without being in contact with a cooling surface on which the condensed moisture may be deposited, a slight cloud or fog of minute drops of condensed water may form in the cooled

air, or, in the absence of nuclei on which condensation can take place, there may be supersaturation.

#### 4. Determination of Relative Humidity from Knowledge of Dew-Point

The absorption method described above leaves nothing to be desired so far as accuracy is concerned, but it is a somewhat tedious and difficult process; and, as it is very often necessary, for meteorological and other purposes, to know the hygrometric state of the air at the actual instant considered and not the mean hygrometric state during, say, an hour, simpler methods based on the determination of the *dew-point* have been adopted.

Since water vapour obeys Boyle's law approximately, even up to saturation, the mass of water present per unit volume is approximately proportional to the pressure it exerts; and this is the saturation pressure at the dew-point. The following may be adopted therefore as an alternative definition of relative humidity:—

The relative humidity of the air at a given instant is equal to the ratio of the maximum vapour pressure at the temperature of the dew-point to the maximum vapour pressure at the actual temperature of the air: *i.e.*

$$\text{R.H.} = \frac{\text{Maximum pressure of water vapour at the dew point}}{\text{Maximum pressure of water vapour at the temp. of the air}}.$$

If  $m$  = mass of water vapour actually present in the air,  $M$  = mass of water vapour necessary to saturate the air under the existing conditions,  $f$  = maximum pressure of water vapour at the dew-point, and  $F$  = maximum pressure of water vapour at the temperature of the air, then—

$$\text{Relative humidity} = \frac{m}{M} = \frac{f}{F}.$$

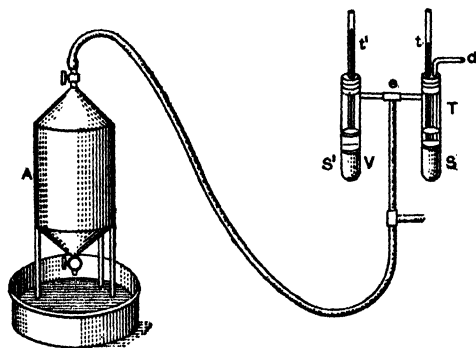


FIG. 138.

Tables have been drawn up (see Table XVI., page 399) showing the maximum pressure of aqueous vapour ( $f$ ) and the mass of vapour present in a given volume of air ( $m$ ) for various temperatures. It will be seen that the numbers in the two columns are very nearly proportional to each other. They are not quite proportional, for unsaturated vapours only obey the gaseous laws approximately. The proportionality is, however, sufficiently close for all practical purposes.

*Experiment. Determine the dew-point and calculate the relative humidity of the air.*—Half fill a thin glass vessel, plain ruby or green, with water. Add small pieces of ice, stir with a thermometer and note the temperature when a deposit of moisture begins to show on the outside of the vessel. This is the dew-point. Check it by withdrawing the ice and allowing the temperature to rise, noting the temperature at which the last traces of dew vanish. Take the mean of the two readings as the dew-point. Dry the thermometer and note the temperature of the air. Look up the saturation pressures at these temperatures in the Table and calculate the relative humidity. Thus, if the dew-point is  $10^{\circ}\text{C.}$  and the air temperature is  $15^{\circ}\text{C.}$ ,

$$\text{R. H.} = \frac{\text{maximum pressure of water vapour at } 10^{\circ}\text{C.}}{\text{maximum pressure of water vapour at } 15^{\circ}\text{C.}}$$

$$\therefore \text{R.H.} = \frac{9.1}{12.7} = 0.72, \text{ or } 72 \text{ per cent.}$$

## 5. Dew-Point Hygrometers

These are instruments devised for determining the dew-point, and thus, as explained above, indicating the hygrometric state of the air. They assume somewhat different forms, but the principle of action is the same in each. The more important forms are given below:—

**REGNAULT'S HYGROMETER.**—This consists of a glass tube, T (Fig. 138), closed below by a thin silver cap, S. Its mouth is fitted with an india-rubber stopper carrying a thermometer,  $t$ , and a piece of glass tubing,  $d$ , both passing down nearly to the bottom of the tube. To use the instrument ether is placed in the tube, and a current of air is drawn through by the aspirator, A. The aspirator should be placed a considerable distance away from the hygrometer, so that the water in the pan may not alter the hygrometric state of



the air near the instrument. Entering by *d*, the air bubbles through the ether in S and enters A after passing through the side tube, *e*, and the vertical tube, V. This passage of air through the ether causes rapid evaporation to take place; the temperature of the liquid therefore falls, and ultimately the aqueous vapour in the air condenses on the surface of S. The temperature is then read. This will be below the dew-point, as no dew is seen until a perceptible quantity has formed. The aspirator is now shut off; the temperature of S rises, and when the last trace of dew vanishes the temperature is again read. The mean of the readings is the dew-point.

By regulating the current of air the cooling of the liquid in S may be made sufficiently slow to note, with accuracy, the temperature at which the film of moisture commences to form on S. Usually this observation is facilitated by having a second tube, S', similar to the hygrometer tube, supported on the same stand in such a position that the appearance of the two silver caps may be contrasted easily, and the dimness due to the deposition of moisture on S detected more readily: S' is not, however, an essential part of the instrument.

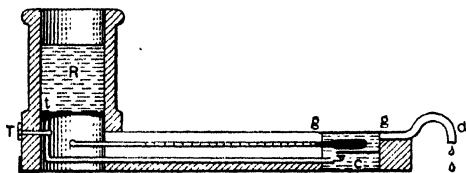


FIG. 139.

The thermometer, *t'*, is convenient for giving

the temperature of the air.

In order to obtain good determinations with any form of dew-point hygrometer, the experiment should be repeated until the temperatures of appearance and disappearance of the film of moisture on the cold surface are very nearly the same, say within  $0.5^{\circ}$  C. of each other. The observations should be made by means of a telescope at some distance from the apparatus, so that all risk of error due to the proximity of the observer is obviated. If a telescope is not available the observer should place a large sheet of glass between himself and the instrument. If a fine wire is drawn over the surface of the silver cap it is easy to detect the first traces of moisture.

**DINE'S HYGROMETER.**—This is a simple and convenient form of hygrometer. R is a small reservoir (Fig. 139), which communicates, by means of a tube, *t*, with the lower compartment of a small double chamber, C; in the upper compartment is placed the bulb

of a thermometer. The stem of the thermometer is visible from above through a narrow groove cut in the stand, and the chamber, C, is covered by a piece of thin black glass, *gg*, on which the slightest film of moisture is perceived easily. To determine the dew-point cold water, containing ice if necessary, is put in R and a slow stream is allowed to flow through C, around the thermometer, under the black glass, and out at *d*. The glass is thus cooled, and when its temperature reaches the dew-point it becomes dimmed with dew. The flow is then stopped, and the temperature, when the dimness just vanishes, is read. The experiment is then repeated as with Regnault's hygrometer.

In another form of Dine's instrument two reservoirs are used, one containing cold water, the other water at the air temperature. Better results are thus obtained.

**DANIELL'S HYGROMETER.**—This is the oldest and most objectionable form of hygrometer, and has now been generally superseded by the others. In principle it is a simple modification of the cryophorus (page 194), containing ether instead of water. One of the bulbs, A (Fig. 140), is made of black glass, or has a zone of gilding round it, and contains a small thermometer, *t*; the other, B, is a plain glass bulb. The tube and attached bulbs are mounted on a suitable stand carrying a thermometer, T, which serves to indicate the temperature of the air.

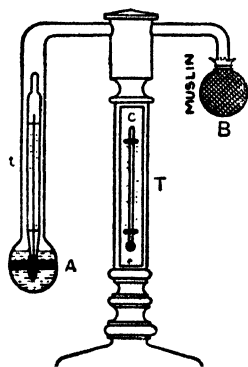


FIG. 140.

To use the instrument, all the ether is passed into A, and B is covered with muslin. A small quantity of ether is poured on this muslin, from which it evaporates rapidly, and, in so doing, absorbs heat from B. The cold thus produced tends to condense the ether vapour in B; this causes rapid evaporation from the surface of the liquid in A, and consequently the temperature indicated by the thermometer, *t*, falls rapidly. As this proceeds the surface of A is watched carefully, and the temperature given by *t* at which dew begins to form on it is noted. The instrument is now left until the dew thus formed on A disappears entirely, and the reading of *t* at the instant of disappearance is recorded. The dew-point is given

very approximately by the mean of the two readings thus taken. The temperature of the air is given by the thermometer,  $T$ , and thus data for the determination of relative humidity are obtained.

It should be noticed that, in this instrument, the cold produced by evaporation is utilised in two distinct ways: (1) in condensing the ether vapour in B, and thus causing evaporation of the liquid in A, and (2) in cooling the bulb A, so that the moisture of the air may be deposited upon it as dew, when the temperature of saturation (dew-point) is reached.

The disadvantages of this instrument are: (1) the hygrometric state of the air is disturbed by the ether vapour around B and by the proximity of the observer, (2) the thermometer,  $t$ , does not indicate correctly the temperature of the surface of A, for the liquid in A is at rest.

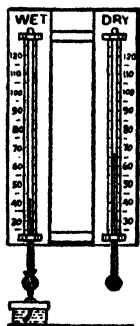


FIG. 141.

#### 6. Wet and Dry Bulb Hygrometer

This instrument is sometimes called *Mason's hygrometer*. It consists of two exactly similar thermometers (Fig. 141), mounted on the same stand in such a way that air can circulate freely round the bulbs. One thermometer is used merely to give the temperature of the air; the other has its bulb covered with muslin, which is kept moist by means of an attached wick communicating with a vessel of water. The wick should be boiled in washing soda to remove grease and then in water before being attached. The evaporation which takes place from this wet bulb produces a fall of temperature, and consequently the wet bulb thermometer always reads lower than the dry bulb.

Now, it is evident that this difference of temperature between the two thermometers, depending, as it does, on the cold produced by evaporation from the wet bulb, will be proportional to the rate at which evaporation takes place, and, as this depends on the quantity of moisture already in the air, it can be seen that the difference of temperature of the thermometers is related indirectly to the hygrometric state of the air. If this relation can be found it may serve to determine the humidity of the air, but, as the assumptions involved are somewhat doubtful, it is usual to determine the dew-point from the thermometric readings by means of tables constructed empirically from the simultaneous indications of a dew-point instrument.

In one such table (Table XVII., page 399), which is due to **Glaisher**, the relation used in calculating the dew-point is

$$t - d = A (t - t_1),$$

where  $t^\circ$ ,  $t_1^\circ$ , and  $d^\circ$  F. are, the temperatures of the dry bulb, wet bulb, and dew-point respectively, and  $A$  is a factor which depends on the temperature of the dry bulb. The values of  $A$  were determined by **Glaisher** from the comparison of thousands of simultaneous observations made with the wet and dry bulb thermometers and Daniell's hygrometer at widely varying temperatures. Transposing the relation given above (note that temperatures are *Fahrenheit*):—

$$\text{Dew point} = d = t - A (t - t_1).$$

Another table—the **Smithsonian table** (Table XVIII., page 400)—is on a different plan. To use it the temperature readings must be converted to the Centigrade scale. From the top line look out the *difference* between the wet and dry bulb temperatures, follow down the column under this, and pick out the number that is on the same line as the air or dry bulb temperature in the first column. This number is  $f$ , the pressure in mm. of the water vapour actually present in the air at the time of observation. The second column, under difference,  $o$ , gives the saturation pressures of aqueous vapour at the temperatures indicated in the first column. Hence, look down the column under difference,  $o$ , for the number equal to  $f$ : the temperature beside this is the dew-point. Interpolation may be necessary.

Yet another method—known as **Apjohn's Formulae**—has been used. Let  $d^\circ$  F. = *difference* in readings of the wet and dry bulb thermometers,  $h$  = barometer reading *in inches*,  $w$  = maximum pressure of water vapour *in inches* corresponding to the temperature of the wet bulb (got from tables), and  $x$  = maximum pressure of water vapour *in inches* at the dew point. Then:—

$$(1) \text{ Wet bulb above } 32^\circ \text{ F.} \quad x = w - \frac{d}{87} \cdot \frac{h}{30}$$

$$(2) \text{ Wet bulb below } 32^\circ \text{ F.} \quad x = w - \frac{d}{96} \cdot \frac{h}{30}$$

from which  $x$  is determined and the dew-point found from tables.

The humidity given by these formulae is generally too great, especially in dry or calm weather, chiefly because the air is never probably quite saturated by contact with the wet bulb.

### 7. The Mass of a Given Volume of Moist Air

To calculate this the following two facts are required:—(1) The mass of one litre of dry air at  $0^{\circ}\text{C}$ . and a pressure of 760 mm. of mercury is 1.293 grm. (2) The mass of one litre of water vapour at any ordinary temperature and pressure is approximately  $\frac{5}{8}$  of the mass of one litre of dry air at the same temperature and pressure.

Consider a volume of  $V$  litres of moist air at pressure  $P$  mm. and temperature  $t^{\circ}\text{C}$ ., and let  $f$  mm. denote the pressure exerted by the aqueous vapour present. The entire gaseous mass may be considered to be made up of two parts:

(a) A volume  $V$  litres of dry air at pressure  $(P - f)$  mm. and temperature  $t^{\circ}\text{C}$ ., the mass of which is given by

$$M' = V \times 1.293 \times \frac{273}{273 + t} \times \frac{P - f}{760} \text{ grm.}$$

(b) A volume  $V$  litres of water vapour at pressure  $f$  mm. and temperature  $t^{\circ}\text{C}$ ., the mass of which is given by

$$m = \frac{5}{8} \left( V \times 1.293 \times \frac{273}{273 + t} \times \frac{f}{760} \right) \text{ grm.}$$

Hence, the total mass  $M$  of the volume  $V$  litres of moist air is given by  $M = M' + m$ . Thus:—

$$\begin{aligned} M &= \frac{V \times 1.293 \times 273}{(273 + t) \times 760} \{ (P - f) + \frac{5}{8} f \} \text{ grm.} \\ &= \frac{V \times 1.293 \times 273}{(273 + t) \times 760} (P - \frac{3}{8} f) \text{ grm.,} \end{aligned}$$

which is less than the mass the air would have if dry.

*Experiment.* Use the hygrometers described above to determine the dew-point and the relative humidity of the air. Also find the mass of, and the mass of water vapour in, a cubic metre of the air. *Observe* the dew-point,  $d^{\circ}\text{C}$ ., the readings of the dry and wet bulb thermometers,  $t^{\circ}\text{C}$ ., and  $t'^{\circ}\text{C}$ ., the height of the barometer,  $H$  mm., and its temperature,  $t^{\circ}\text{C}$ .

*Example.*—The following data were obtained in carrying out the above experiment:—

*Wet and dry bulb hygrometer:* Temperature, wet bulb  $12^{\circ}\text{C}$ ., dry bulb  $15^{\circ}\text{C}$ .

*Regnault's hygrometer:* Appearance of dew on cooling,  $9.5^{\circ}\text{C}$ . Disappearance of dew on warming,  $10.5^{\circ}\text{C}$ .

*Barometer:* Height 774.1 mm., Temperature 15° C., Brass scale.

(A) CALCULATION OF DEW-POINT.—

(1) *From Regnault's hygrometer:* Dew-point =  $\frac{1}{2}(9.5 + 10.5) = 10^{\circ}\text{C.}$

(2) *From wet and dry bulb hygrometer:*

(a) From Table XVIII., page 400. Difference in temperature between wet and dry bulb = 3° C.;  $\therefore$  saturation pressure =  $\frac{1}{2}(8.3 + 9.7) = 9.0\text{ mm.}$

Hence, the dew-point =  $8.0 + \frac{1.0}{1.2} \times 2.0 = 9.7^{\circ}\text{C.}$

(b) From Table XVII., page 399, Dry bulb reading = 15° C. = 59° F. Wet bulb reading = 12° C. = 53.6° F. Hence—

$$59 - d = 1.89(59 - 53.6) = 10.2;$$

$$\therefore d = 49^{\circ}\text{F.} = 9.5^{\circ}\text{C.}$$

The average value of the dew-point is the mean of the three results above  
= 9.7° C.

(B) CALCULATION OF RELATIVE HUMIDITY. (Table XVI., page 399.)—

Maximum vapour pressure at the air temperature, 15° C. = 12.7 mm.

Maximum vapour pressure at the dew point, 9.7° C. = 8.9 mm.

Therefore, relative humidity =  $\frac{8.9}{12.7} = 0.70 = 70\text{ per cent.}$

(C) CALCULATION OF MASS OF A CUBIC METRE OF MOIST AIR.—

Height of barometer, corrected to 0° C. = 774.1 (1 - 0.000162  $\times$  15)  
= 772.2 mm.

Total pressure = 772.2 mm. The vapour pressure = 8.9 mm.

Therefore, the pressure of the dry air = 772.2 - 8.9 = 763.3 mm.

Mass of the dry air =  $1293 \times \frac{273}{288} \times \frac{763.3}{760} = 1231\text{ grm.}$

Mass of the water vapour =  $\frac{5}{8} \times 1293 \times \frac{273}{288} \times \frac{8.9}{760} = 9\text{ grm.};$

$\therefore$  Total mass = 1240 grm.

## 8. Hygrosopes

Hygrosopes are contrivances which serve to indicate the humidity of the air by means of some physical effect produced by the absorption of moisture by hair, catgut, etc.

Many substances absorb moisture to a degree dependent on the quantity present in the air, and generally this absorption is accompanied by some variation in the form or condition of the substance. The nature of the variation depends on the structure of the substance; membranous bodies, such as paper, parchment, etc., expand or contract according as they absorb or lose moisture; filamentous substances change much more in thickness than in length; ropes, strings, and threads, which are composed of twisted fibres, swell out and shorten on the absorption of moisture. The individual fibres of a rope, etc., probably increase *slightly* in length, but the

rope, as a whole, shortens for the same reason that a number of thick strings form, on twisting, a shorter rope than the same number of fine strings of the same length twisted to the same extent. Hair, owing to its peculiar structure, shortens as the humidity increases. A single hair is made up of a series of cones fitting one into the other; on absorption of moisture it swells out, and the vertical angles of the cones increase. Consequently the cones become flatter and the length of the hair decreases.

*Saussure's hygroscope* (Fig. 142) is mainly of historic interest as being the first instrument designed for hygrometric purposes. It consists of a clean, grease-free hair fastened at the top to a screw-pin: the lower end passes once round a pulley (to which a pointer

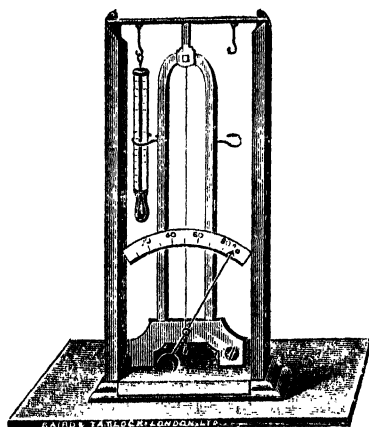


FIG. 142.

is attached) and carries a small weight. Changes in the length of the hair corresponding to changes in the humidity of the air cause the needle to be deflected over a scale graduated to indicate various degrees of humidity, but the indications are relative only, and the instrument is never used for accurate work.

## 9. Formation of Cloud and Rain

Clouds are formed by local condensation of the water vapour present in the air in the upper regions of the atmos-

phere. They consist chiefly of very minute drops of water which, on account of their small size, fall very slowly through the air.

One method of cloud formation is illustrated by the experiment on page 206 (Fig. 136). The jet of steam issuing from the flask supplies water vapour more rapidly than it can be distributed throughout the air by diffusion. Hence in the region of excess supply, the vapour condenses and forms a small "cloud."

In nature, this process of cloud formation occurs sometimes, but it is by no means the commonest process. It is well known that if the pressure on a gas is reduced the volume increases, and that if no heat is passed into the gas from without the gas becomes colder, and if the process is carried far enough any water vapour in

the gas separates out in minute drops. Thus if a little water be placed in a large flask, the flask shaken so that the air in the flask becomes saturated with water vapour, and then the flask be exhausted quickly, the interior fills with mist.

In nature, cooling of air consequent on decrease of pressure occurs when a mass of air leaves the surface of the earth and ascends to upper regions. At first cloud is formed and ultimately rain is produced. In fact, some meteorologists regard an ascending current of air as necessary for the production of a measurable rainfall. Cases where clouds and rain are being formed continuously by this means are seen on the mountainous west coast of South America. The prevailing westerly winds laden with moisture, as they travel up the mountain sides, rapidly reach regions of low atmospheric pressure and the water separates out, giving a copious rainfall. The same occurs to a less extent when south-westerly winds laden with water vapour from the Atlantic ocean meet the hills of N.W. and S.W. England and Wales.

It should be specially noted that cloud really marks a region of condensation which is fed by vapour, and is limited in extent by continuous vaporisation and diffusion from its outer surface. The cloud is therefore not a floating mass of unchanging material, but a constantly changing mass of condensed vapour, which is formed continuously by condensation in the condensation region, and is dissipated as rapidly by vaporisation and diffusion at its outer surface. A cloud therefore cannot be said to float; it is merely a formation marking any region in which the conditions which determine condensation may obtain.

The great variety of cloud-forms is due to the various conditions under which they are formed. By the methods indicated above, huge clouds known as **cumulus** clouds form at the top of the ascending column. Similarly, when currents of air at different temperatures meet, the layers of contact may become regions of condensation, and clouds, often of the **stratus** type, may form in these regions. In the case of clouds formed at great heights, where the temperature is very low, the constituent drops may be frozen into small ice particles, or the vapour may be condensed in minute ice crystals, forming the beautiful clouds known as **cirrus** clouds. The dark rain clouds of cumulus-like structure are called **nimbus** clouds.

If the lower layers of air are saturated, the small cloud particles collect into drops and fall as **rain**. If the cold is sufficiently intense



to freeze the minute particles before they collect into rain-drops, a fall of snow results. If the rain-drops form and are then frozen, the result is hail.

## 10. Formation of Fog or Mist, and Haze

When the vapour in the air condenses in regions at or near the surface of the earth, fog or mist is produced. The mode of formation of fog is almost the same as in the case of a cloud, the difference in the appearance of the phenomena being due mainly to the fact that clouds are formed at considerable heights above the observer, while fogs and mists are formed near the surface of the earth. In the case of fog, however, the masses of air involved are often at rest or in very slow motion, and the bank of fog produced is more stationary and fixed in form than a cloud usually is.

The most frequent cause of fog is the cooling of the air below the dew-point. For example, the fog region near Newfoundland is due to the cooling of the warm vapour-laden wind from over the Gulf Stream by the cold air of the Labrador current. Similarly, when warm saturated air flows up a mountain side, the cooling consequent on the expansion produces a thick mist around the mountain top.

Fogs often form in river valleys and over lakes. If the water is warmer than the air, a fog is formed by the excess supply of vapour from its surface. If, however, the water is colder than the air, the layers of air in contact with it are cooled below the dew-point, and a fog or mist appears.

The formation of fog is facilitated greatly by the presence of small particles of matter in the air. Indeed, nuclei of some-kind are essential as centres of condensation for the formation of a fog. This explains the frequency of dense fogs in large towns. The smoke and dust particles in the air serve as convenient centres of condensation, so that directly the air is cooled below the dew-point, a fog composed of comparatively large drops of water with a core of soot or dust is produced.

To meteorological observers the words fog, mist, haze, indicate a deterioration of the transparency of the lower regions of the atmosphere caused by solid or liquid particles. Mist and fog refer to surface cloud, and the air is saturated with water vapour when they occur. A slight fog is sometimes called a haze, but it is better to confine the term haze to the obscurity caused by smoke, dust, or other cause when the air is dry. In large cities, the smoky

surface cloud which occurs when the air is calm and dry is usually called a fog; it would be better termed a thick haze.

Some draw a distinction between mist and fog by regarding a mist as a surface cloud which wets objects exposed to it, and a fog as a surface cloud which does not wet exposed objects. The distinction is scarcely practical, however. Fog seems always to imply inconvenience to travellers, and it is in this sense that the term may be used most safely; the same cloud may be a fog to a person travelling in it, and a mist to a person looking at it from a distance.

## II. Formation of Dew

A satisfactory theory of the formation of dew was first given by *Wells*. During the day objects on the surface of the earth are heated by direct radiation (see Chapter XVII.), and the air in contact with them is also heated, and generally contains a large quantity of water vapour. During the evening cooling takes place, and the substances which radiate well cool quickly below the temperature of the surrounding air. As a consequence the air in contact with these bodies cools also, and ultimately the dew-point (Art. 3) is reached at which the air is saturated with the vapour it contains, and, if further cooling takes place, a portion of the vapour is deposited as dew on the surfaces of the adjacent bodies.

On this theory, it is evident that the conditions necessary for a copious deposition of dew are: (1) a clear sky, to allow free radiation into space; (2) a calm state of the atmosphere, in order that the air in contact with any object may remain in position until cooled below the dew-point; (3) the objects on which dew is deposited must be (a) good radiators, in order that they may cool rapidly, (b) bad conductors, in order that the loss of heat by radiation may not be counterbalanced by a gain of heat from the earth by conduction—if the object is isolated and of small size, it does not matter whether it is conducting or not, (c) placed near the earth. When the object is some distance above the earth, the air in contact with it, on being cooled, sinks towards the earth and its place is supplied by warmer air from above. Thus none of the air which comes in contact with the object may be cooled sufficiently to deposit its vapour as dew.

For example, it is often found that certain objects are quite wet with dew, while neighbouring ones are quite free from it. Grass is always more heavily bedewed than gravel or pebbles in its vicinity, and a polished metallic surface may remain quite dry among the

dewy grass. The explanation of this is that grass radiates well, loses its heat quickly, and thus lowers considerably the temperature of the overlying air. Gravel, pebbles, and polished surfaces do not radiate so freely, and may not become cold enough to reduce the temperature of the air above them to the dew-point.

The temperature of the surface of a large body embedded in the ground will also depend on its conductivity; for as the top surface is cooled by radiation heat will flow to it from the interior which is at a higher temperature. Thus it is seen that the largest quantities of dew are formed on bodies which are good radiators and bad conductors.

Wells' theory has been confirmed by recent investigation, but other experiments have shown that dew is derived not only from vapour present in the air, but also from vapour arising from the earth and from the vegetation on which the dew is formed.

## 12. Formation of Hoar-Frost, Rime, and Glazed Frost

**Hoar-frost** resembles dew in its mode of formation. If the objects on which the dew is deposited are below  $0^{\circ}\text{C.}$ , the water freezes at once, and the projecting edges of the objects are outlined in tiny ice crystals. This constitutes hoar-frost.

**Rime** is an accumulation of frozen moisture on trees and exposed objects, which thus present a silvery-white and rough appearance. It bears some resemblance to hoar-frost, but rime occurs only in a fog, whilst hoar-frost occurs on a clear night. The white deposit on grass which is often seen on cold foggy mornings is not rime, but hoar-frost formed before the development of the fog.

**Glazed frost** is a transparent glass-like coating of ice covering trees, buildings, etc. It is caused usually by rain which freezes as it reaches the ground. It may occur also when a warm moist air current sets in suddenly after intense cold; the moisture of the air separates out on cold surfaces and coats them with ice.

## CHAPTER XII

### THE MECHANICAL EQUIVALENT OF HEAT. THE FIRST LAW OF THERMODYNAMICS

THERE is reason to believe that the particles of every body, whether solid, liquid, or gas, are in perpetual vibration.

Indeed, the heat which bodies possess and emit is most probably due to the vibrations of their particles. Owing to their vibrations these particles possess kinetic energy, and it is assumed that what is called heat is due to this energy (page 3).

#### 1. Energy

Energy can be transferred from one body to another. Impact is one method. If a billiard ball in motion strikes one at rest, the latter begins to move whilst the former either stops or moves on with diminished speed. Thus the ball which had no energy before the impact possesses energy after the impact, whilst the ball originally in motion loses all or part of its energy.

A more common way of bringing about such a transfer of energy is illustrated by holding in the hand one end of a strong string to which a weight is attached. If the hand is moved to and fro in a horizontal line, no particle of the string moves, except to vibrate in a horizontal line, but the movement passes along the string in the form of waves until the particles near the weight, and finally the weight itself, are set in motion. Thus, without the transfer of any *material* from the hand to the weight, motion, and therefore kinetic energy, has been transferred by vibrating an intermediate medium.

It was found convenient by the early scientists to postulate the existence of an imaginary medium, called the **ether**, which filled all space and which was capable of carrying energy from one body to another. It was then considered that the energy of the sun is transferred to us by means of a wave motion in this intervening medium, and makes itself sensible as heat and light (page 331). While it is not possible to demonstrate by experiment the existence of this medium (and many scientists now "ignore" it), the *assumption* of its existence provides a means, particularly for the beginner, of visualising the transmission of energy through space. Moreover,

the mathematical theory and the "properties" of this imaginary medium have been investigated fully.

It is now held firmly that not only heat, but also light and sound are merely forms of energy. Great experimenters have shown that (1) any one form of energy can be converted into any other, and (2) in such a conversion, the quantity of the one used up is invariably equal to the quantity of the other created. It is not difficult to show the transformation from one form to another by simple experiment, but to show the strict equality between the quantities used and created requires special apparatus. The subject of the transformation of work into heat and *vice versa* will be treated in detail below.

## 2. The Dynamical Theory of Heat

It has already been stated that heat is a form of energy, and it has been established that a given quantity of heat, measured in any arbitrary units, has a definite and constant equivalent in mechanical work or energy, measured in mechanical units such as foot-pounds or ergs. The experiments and arguments which establish the truth of this *dynamical theory* of heat will now be sketched briefly.

Up to the commencement of the last century heat was considered to be a material igneous fluid, called *caloric*, which rendered a substance hot or cold according as it was present in that substance in large or small quantities. When it was shown that heat could be produced by friction, percussion, or other mechanical means, this was explained by assuming that these mechanical actions changed the condition of some portion of the substance, and thus diminished its capacity for heat; or, some of the caloric was forced out of the substance and made to appear as sensible heat.

The dynamical theory of heat was established by two distinct steps. Towards the close of the eighteenth century, the experiments of *Rumford* and *Davy* showed that heat could not be a *material* substance, and thus the old caloric theory of heat was disproved. However, this theory still held the field until, in 1849, the results of *Joule's* quantitative experiments established the *equivalence of heat and work*, and proved that *heat must be a form of energy*. Later experiments by other workers and the mathematical development of the subject by *Rankine*, *Thomson* (Lord Kelvin), and *Clausius* entirely confirmed this result, and completely established the dynamical theory.

### 3. Rumford's Experiments

Rumford was an Anglo-American in the employ of the Bavarian government, and was led to experiment on this subject whilst superintending the boring of cannon at the Munich arsenal. It was noticed that during boring a large amount of heat was developed both in the cannon and in the boring tool, and, struck with the apparently unlimited supply of heat, he determined to find out whether heat really was a material fluid, caloric, as it was then considered to be.

In considering the method of experiment, it occurred to Rumford that if the heat was forced out of any part of the system dealt with, it came most probably from the borings, and accordingly he decided to determine whether there was any difference between the specific heat of the borings and that of the solid metal. This was done by taking equal weights of each, heating them to  $212^{\circ}$  F., and then immersing them in equal quantities of water at the same temperature. After one minute the rise of temperature in each case was the same, and the conclusion was reached that the heat produced could not have been furnished at the expense of the borings. Rumford then decided to use a *blunt* borer, so that only a very small quantity of borings should be produced in a given time. Apparatus was arranged for this experiment, and an enormous quantity of heat was still evolved, although the weight of the borings produced was only about one-thousandth of that of the whole apparatus. Rumford now was thoroughly convinced that the heat could not come from the borings; neither could it come from any other part of the apparatus, for the metal was still in its initial condition and therefore must have the same specific heat, and every part of the system was *gaining* heat instead of losing it.

It then occurred to him that the only other source from which the heat could come was from the air. Accordingly the air was excluded by causing the boring to take place under water. In  $2\frac{1}{2}$  hours from the commencement of the experiment the water boiled. This heat, it was argued, could not have come from the water, for the only change of condition experienced by the water was that due to *gain* of heat.

From all these experiments Rumford came to the conclusion that heat was *not* a material substance. In a paper published in 1798 the case was stated thus: "Anything which any insulated body, or system of bodies, can continue to furnish *without limitation* cannot possibly be a *material substance*; and it appears to me to be

extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being excited or communicated in these experiments except it be *motion*."

#### 4. Davy's Experiments

In 1798, Davy showed that when two pieces of ice are rubbed together in a vacuum the ice melts, even if the initial temperature of the ice and its surroundings be some degrees below the freezing point. The melting of the ice shows that heat is produced, and its production cannot be due to a diminution of thermal capacity, for the specific heat of the water produced is *greater* than that of the ice. Davy did not see the full significance of this result at the time, and it was not until 1812 that he stated clearly his opinion that heat was a form of molecular energy.

Many simple experiments may be carried out to show that the mechanical work expended in impact, friction, etc., has been transformed into heat:—

(a) Hammer a piece of lead, saw wood, etc., and take the temperature of the lead, saw, etc., before and after the experiment. It will be found that the temperature has risen.

(b) Rub a brass nail or button on a piece of wood, and notice its increase of temperature.

(c) Bore a hole in a piece of hard wood with a bradawl. The bradawl becomes hot.

(d) Feel the axle of a wheel which has been rotating rapidly. It is warm, possibly hot.

(e) Take a piece of thin iron plate and bend it backwards and forwards to produce fracture along a certain line. Feel the metal at this line. It is hot.

(f) Use a bicycle pump to inflate a tyre or to pump air into a closed vessel. Note that the pump becomes warm. Part of this is due to friction between the piston and the barrel; but the greater part is due to the heat developed in the air on compression. To test this point, work the pump with the nozzle open; the pump becomes only slightly warm.

(g) Blow air by a pair of bellows against the face of a thermopile. The indication of the galvanometer shows that the temperature of the air has risen by reason of the work done upon it.

(h) Allow compressed air to expand from a cylinder in which it has been compressed. Cooling occurs.

(i) Study a steam engine. Note the transformation of the energy of the heat of the burning coals into the energy of mechanical motion.

#### 5. Joule's Experiments

It was not until 1849 that the dynamical theory was generally accepted. In that year, Joule, of Manchester, completed a series

of experiments which showed not only that heat was a form of energy, but determined accurately the quantitative relation between a given quantity of mechanical energy and the equivalent quantity of heat.

Joule's most important experiments were on the development of heat by fluid friction and on the heat effects associated with the compression and expansion of gases. Some of these experiments will now be described.

(I) JOULE'S EARLIER EXPERIMENTS ON FLUID FRICTION.—These experiments consisted in the development of heat by churning water in a copper vessel by means of a suitable paddle. The friction of the water on itself and on the surfaces of the vessel and paddle

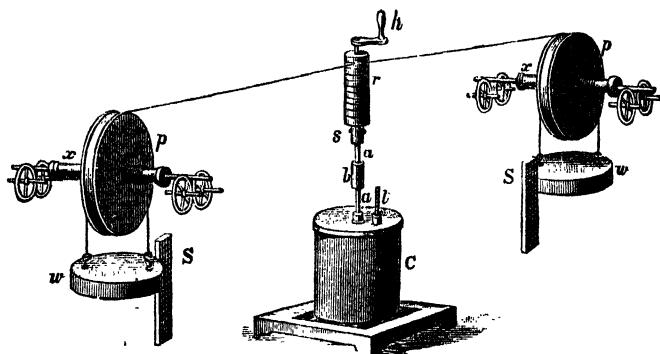


FIG. 143.

produced heat, which resulted in an appreciable rise in the temperature of the water. In the apparatus used in the first experiments, C (Fig. 143) represents the vessel containing the water. It was made of copper, 10 in. high and 7 in. in diameter, and was capable of containing about 10 lb. of water. Inside it were fixed four vanes or partitions, P (Fig. 144). The vanes were attached to the brass framework which supported the sockets for the axle of the paddle, in such a way as to leave a free central space in which this axle revolved. The paddle consisted of a central axle, *aa* (Fig. 144), carrying eight sets of brass vanes, V, fixed at equal angles. The axle revolved in two sockets at the top and bottom of the vessel, C, and the revolving vanes, V, passed through spaces cut in the stationary partitions, P. By this arrangement the water was prevented from rotating in the direction of revolution of the paddle.



The motion of the paddle was produced by the fall of two equal lead weights,  $ww$ , each either 10 lb. or 30 lb., attached by strings to the equal axles,  $xx$ , 2 in. in diameter, of two exactly similar and equal wooden pulleys,  $pp$ , 1 ft. in diameter. The motion thus communicated to the axles was transmitted by the pulleys, by means of cords, to the vertical wooden spindle,  $r$ , attached to the upper part of the paddle axle. To diminish friction as much as possible, the pivots of the pulleys were of steel and rested each on two steel friction wheels. The handle,  $h$ , was used to wind up the weights into the position shown; by taking out the pin at  $s$ , the spindle,  $r$ , could be disconnected from the axle,  $aa$ , and the weights could thus be wound up without causing rotation of the paddle.

With this apparatus Joule set himself to determine the quantity of heat produced by the expenditure of a given amount of energy.

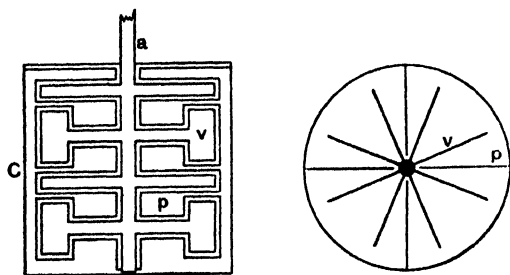


FIG. 144.

For this purpose the water equivalent of  $C$  and its accessories was determined, and a known quantity of water was placed in  $C$ . The temperature of this water was given by a very delicate thermometer,  $t$ , reading to  $\frac{1}{100}^{\circ}$  F.

To prevent loss of heat from  $C$ , it was placed on a wooden grating which touched the ground only at the four corners, and the axle,  $aa$ , which was of brass, was made in two pieces joined at  $b$  by a piece of wood. These precautions helped to prevent loss of heat by *conduction*.

The weights were wound up, the pin at  $s$  placed in position, and, the temperature indicated by  $t$  having been read, the weights were allowed to fall to the ground, the distance being about 5 ft. This was repeated 20 times with as little delay as possible, and the final temperature of the water in  $C$  was then taken carefully. It was noticed that the velocity of the weights during the latter half of their fall was nearly uniform. The velocity was determined with some accuracy by repeated observation. The data thus obtained, subject to a few corrections, served to determine the required relation between the total quantity of work done and the quantity of heat produced by its expenditure.

Let  $m$  denote the mass of each weight,  $h$  the height of its fall, and  $v$  the velocity on reaching the ground; then,

$$w = mgh - \frac{1}{2}mv^2,$$

denotes in absolute units the work done by each weight during each fall, for  $mgh$  is the loss of potential energy of each weight and  $\frac{1}{2}mv^2$  is the gain in kinetic energy of each weight. Hence, if the weights fall  $n$  times, the total work done is  $2nw$ .

Again, let  $t$  denote the rise of temperature indicated by the thermometer, and  $M$  the water equivalent of the apparatus and the water contained; then,

$$Q = Mt,$$

denotes the heat produced by the expenditure of a quantity of work denoted by  $2nw$ .

The quantity,  $2nw$ , is subject to several corrections, the most important of which is that due to the work absorbed by friction outside the water. To determine this correction, Joule disconnected the spindle from the paddle, and connected the weights by a single cord adjusted round  $r$  in such a way that as one weight descended the other was raised. A small weight,  $x$ , was then placed on one of the weights, and adjusted by repeated experiment until the velocity of descent was equal to that noted during an actual experiment. The weight,  $x$ , thus represented approximately the resistance due to friction, and the work spent in overcoming it, for each descent, is given by  $w' = xh$ . Hence the work absorbed by friction during  $n$  descents is given by  $nw'$ , and the total work expended in the production of heat in the water is expressed by  $W = 2nw - nw'$ .

The quantity,  $Q$ , is also subject to an important correction due to the loss of heat by radiation during the 35 minutes occupied by the experiment. This was corrected by noting the rate of cooling for 35 minutes after the completion of the experiment. Let  $q$  denote the loss of heat by radiation; then  $(Q + q)$ , which may be denoted by  $H$ , expresses the total amount of heat produced by  $W$  units of work.

The object of Joule's experiments was to obtain the relation between these two quantities. If  $H$  thermal units of heat are equivalent to  $W$  units of work, then one thermal unit of heat is obviously equivalent to  $W/H$  units of work. Joule determined the value of this ratio from a very large number of experiments. He found it almost *constant*, thus establishing the principle of equivalence

between work and heat, and he gave as the mean value of the ratio

$$\frac{W}{H} = 772,$$

where  $W$  is expressed in foot-pounds and  $H$  in pound-degrees *Fahrenheit*. This means that one pound-degree Fahrenheit of heat is equivalent to 772 foot-pounds of work, or that if 772 foot-pounds of work are expended in the production of heat, the quantity of heat produced will raise one pound of water through one degree Fahrenheit.

The value of this ratio,  $W/H$ , is known as **Joule's equivalent** or the **mechanical equivalent of heat**, and is usually denoted by  $J$ . It is sometimes called the *specific heat of water in mechanical units*, but this is not a good expression for it.

(2) **JOULE'S LATER EXPERIMENTS ON FLUID FRICTION.**—At a

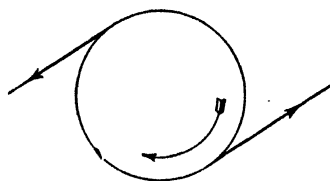


FIG. 145.

later date Joule carried out a final series of experiments for the determination of the mechanical equivalent of heat by the water friction method. These experiments, completed in 1878, were very similar to the earlier experiments in method, but the work done in churning the water in the calorimeter was

measured in a more satisfactory way. The calorimeter, instead of being fixed, was supported so as to be free to rotate with the paddle, but was prevented from so doing by the action of a couple applied by cords attached to the circumference of the calorimeter. The curved arrow (Fig. 145) shows the direction of rotation of the paddle, and it will be seen how the tensions in the cords attached to the calorimeter supply the couple necessary to prevent its rotation with the paddle. The cords are applied to the calorimeter in a horizontal plane, but each cord passes over a pulley and, hanging vertically, carries a weight at the end. The weights are adjusted so as to keep the calorimeter in equilibrium against the couple, due to the rotation of the paddle. Thus, if  $r$  denote the radius of the calorimeter at the section where the cords are applied, and  $M$  the mass attached to each cord, then  $Mg \cdot 2r$  or  $2Mg r$  is the moment of the couple applied by the cords, and, when there is equilibrium, this is equal to the moment of the couple against which the paddle works.

Hence, the work done by the paddle in one revolution is  $2Mgr.2\pi$ , or  $4\pi Mgr$ .

In order that the calorimeter should be supported free, as far as possible, from all constraint preventing its rotation with the paddle, other than that due to the cords, it was supported from below by a stand floating freely in a vessel of water. By adjusting the quantity of water in the vessel, the supporting stand could be made to take almost all the weight of the calorimeter.

A diagram of the apparatus is shown (Fig. 146);  $h$  is the calorimeter,  $vw$  the hydraulic stand,  $d$  and  $e$  the driving wheels,

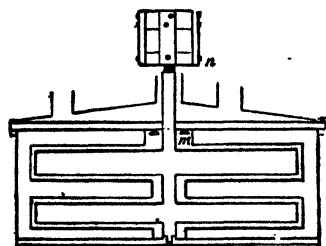


FIG. 147.

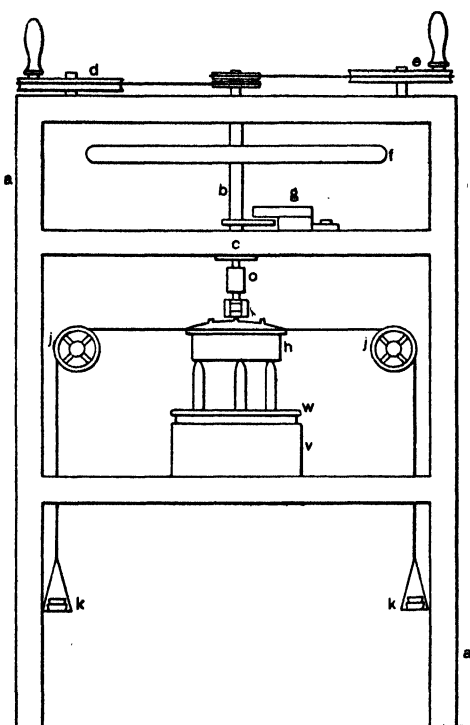


FIG. 146.

$f$  a heavy fly-wheel to secure uniform speed of rotation, and  $g$  a counter for registering the turns made by the paddle. The apparatus was enclosed in a massive wooden box; the top of the box carried the driving wheels, the upper shelf by a bearing at  $c$  carried the weight of the paddle and fly-wheel, and the second shelf carried the hydraulic stand which supported the calorimeter.

The vertical section of the calorimeter and paddle are shown (Fig. 147). The paddle in this case has two sets of vanes, an upper set and a lower set, attached to the axis

of the paddle in such a way that at the instant any paddle vane is in transit through a stationary vane, no other paddle vane is in this transit position, and that the transits during a complete revolution succeed each other at regular intervals. With this arrangement, the resistance to the rotation of the paddle is more uniform, and equilibrium is maintained more easily. In making an experiment, the paddle was rotated for about 35 minutes, and the rise of temperature noted in the usual way. The heat produced in the calorimeter thus could be measured, and the equivalent work was calculated in the way indicated above.

The values obtained by Joule in these experiments varied from 773.1 to 777.7 foot-pounds as the equivalent of one pound-degree *Fahrenheit* of heat. The mean result given finally by Joule as the result of his experiments was 773.4 foot-pounds.

Joule also carried out a series of experiments on the friction of mercury, using a small iron apparatus similar to that described above. The results obtained were almost identical with those obtained by using water, thus proving that the equivalence of heat and work is independent of the nature of the apparatus by which the transformation is effected. This conclusion was confirmed further by the results of experiments with iron plates producing heat by their friction when rubbed together under mercury, and also by experiments on the compression and expansion of gases (Art. 9).

## 6. Rowland's Experiments

Joule's work was considered so important that *Rowland*, of Baltimore, thought it desirable to apply a number of corrections to the data of Joule's experiments, and also to repeat and extend the experiments with the most laborious attention to the details of observation and correction of errors. The more important corrections applied by Rowland to Joule's work included: (1) the reduction of the temperatures recorded in the experiments to air thermometer temperatures, this being done by direct experiment with Joule's thermometers which were available for the purpose; (2) the correction for the variation of the specific heat of water with temperature; (3) the correction of all weighings for the buoyancy of air.

The relative value of these corrections is indicated by the following, applied to one of Joule's results:—Joule's value, 774.6. Thermometer correction, + 3.7; specific heat correction, + 0.2;

buoyancy correction, — 0.9. Corrected value, 777.6 foot-pounds (per *pound-degree Fahrenheit* unit of heat).

In the experiments devised and carried out by Rowland, the method of Joule's later experiments was adopted. The object in view, in designing the apparatus, was to reduce to the lowest limit all the possible sources of error, and to provide for the correction of unavoidable sources of error with maximum of accuracy. In Joule's experiments, the most unsatisfactory element was the large value of the cooling correction relative to the total rise of temperature during an experiment, for this caused an error in the determination of the cooling correction to appear as an appreciable error in the value of  $J$ . Rowland improved on this by arranging to get a much larger rate of rise of temperature, by the expenditure of much more power in driving the paddle. In this way the percentage value of the cooling correction was greatly reduced, for with a given rise of temperature the cooling correction is directly proportional to the

time in which the rise takes place. Thus, in some of Joule's experiments,  $1^{\circ}\text{C}$ . rise of temperature took place in about 1.5 hours; whereas in Rowland's experiments a rise of  $1^{\circ}\text{C}$ . took place in less than two minutes; the cooling correction in Rowland's experiments was therefore only about  $\frac{1}{80}$ th as great as in Joule's experiments.

In Rowland's apparatus (Fig. 148) the calorimeter was suspended by a steel wire. The paddle shaft entered the calorimeter from below and was driven by a steam engine. The cords carrying the

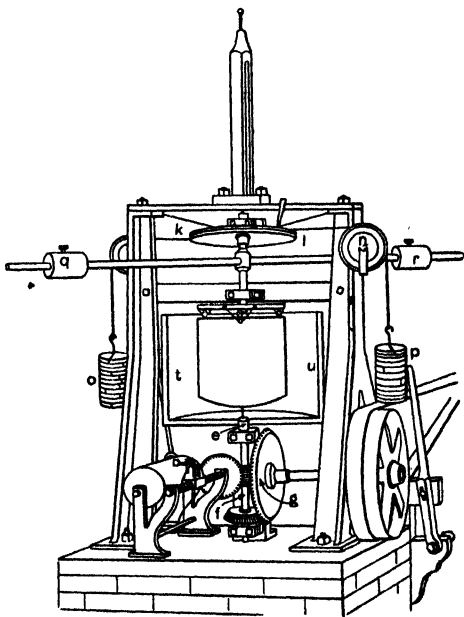


FIG. 148.

balancing weights were attached to the rim of a wheel connected rigidly to the calorimeter. The total balancing couple was thus due partly to the balancing weights and partly to the tension of the wire. The calorimeter and paddle were similar to Joule's, but the number of paddle vanes was increased and arranged so that the thermometer remained in the water all the time, and care was taken to circulate the water past the thermometer bulb. The calorimeter was surrounded by a constant temperature jacket to ensure accurate corrections for cooling.

Rowland gave the mean value of  $J$  from his own experiments as 427.52 *gram-metres per calorie* at  $14.6^{\circ}\text{C}$ . The mean result deduced by Rowland from Joule's experiments was 426.75 *gram-metres per calorie* at  $14.6^{\circ}\text{C}$ . These results differ by less than 0.2 per cent., and give the value of  $J$  as very nearly  $4.19 \times 10^7$  *ergs per gramme degree Centigrade* at about  $15^{\circ}\text{C}$ .

Rowland's experiments showed that the variation of the specific heat of water with temperature has a bearing on the value of  $J$  that comes well within the limits of observation. From results obtained at different temperatures between  $5^{\circ}\text{C}$ . and  $36^{\circ}\text{C}$ ., Rowland was led to conclude that the specific heat of water passes through a minimum at a temperature not far from  $30^{\circ}\text{C}$ ., and this conclusion has been justified subsequently by experiments which go far to show that the specific heat of water reaches a minimum at  $40^{\circ}\text{C}$ . (See page 123.)

## 7. Miculescu's Experiments and Hirn's Experiments

(1) In 1892 *Miculescu* published the results of a determination of  $J$  by a direct method similar to that of Joule and Rowland. The calorimeter was kept at a stationary temperature by the flow of water between its double walls, and the amount of heat developed in a given time measured by determining the rate of flow of the water and the difference between the temperatures of the water at entrance and exit. *Miculescu* gave 426.8 as the number corresponding to Rowland's value, 427.52, quoted above.

(2) *Hirn* found the value of  $J$  by an impact experiment. A large piece of iron was suspended by strings, so that when the strings were vertical the iron rested just against a thick lead cup fitting in the end of a very large stone suspended similarly to the iron. Lead was chosen because of its inelasticity—there is little rebound from lead, and little sound is produced. The iron was drawn aside, and the height it was raised measured. It was then

released. At the impact the energy,  $W_1$ , spent by the experimenter in raising the iron when drawing it aside, less the energy,  $W_2$ , spent against gravity in lifting the stone and iron after the impact, was converted into heat. The temperature of the lead was taken before the impact. After the impact, the lead cup was removed from the stone, water at  $0^\circ \text{C.}$  was poured into the cup, and its final temperature taken. From these readings the heat,  $H$ , generated by the impact was calculated. Thus  $J$  could be evaluated from the relation,  $W_1 - W_2 = JH$ . The result obtained was 425 gram-metres per calorie.

(3) In all the experiments described so far work has been transformed into heat. In 1857, *Hirn* performed a striking experiment with a steam engine, in which heat was transformed into work. The quantity and pressure of the steam entering the cylinder were measured, and from these the heat supplied in a given time,  $H_1$ , was calculated. When the still hot steam left the cylinder, it was made to pass through tanks of cold water, and so the amount of heat,  $H_2$ , remaining in it when it left the cylinder was measured. Also, the heat lost by radiation from the steam boxes and pipes,  $R$ , was measured. The difference,  $H_1 - H_2 - R$ , is equivalent to the work done by the engine in the given time.

The work done by the engine per stroke was measured by an indicator diagram in dynamical units. The mean effective pressure on the piston obtained from the diagram, multiplied by the cross-section of the cylinder and the length of the stroke of the piston, gave the work done per stroke (Art. 9), and this multiplied by the number of strokes in the given time gave the work done,  $W$ , for an amount of heat  $H_1 - H_2 - R$ . Whence,

$$J = \frac{W}{H_1 - H_2 - R}$$

*Hirn's* value of  $J$  by this method was 420 gram-metres per calorie.

## 8. Electrical Experiments

If an electric current of  $I$  amperes passes through a wire, and the resistance of the wire is such that the potential between the ends of the wire is  $V$  volts, it follows that, since the wire is merely an inert portion of a circuit, the electrical energy turned into heat energy in the wire is  $VI$  joules per second. (See *Hutchinson, Advanced Textbook of Magnetism and Electricity.*) It is more usual, however, to express the heat energy in terms of the resistance and



the current. If  $R$  is the resistance of the wire, then by Ohm's law,  $V = IR$  and therefore,  $VI = I^2R$ . Thus, *the heat generated per second in a wire of resistance  $R$  ohms by a current of  $I$  amperes*  $= I^2R$  joules: this is known as **Joule's law**. From this it follows that the heat,  $H$ , developed in a time,  $t$  seconds, in a wire of resistance  $R$  ohms by a current of  $I$  amperes is  $I^2Rt \times 10^7$  ergs. Dividing by  $J$ , this gives:—

$$H = \frac{I^2Rt \times 10^7}{J} \text{ calories.}$$

Hence, if the heat developed is measured in calories, a means of finding  $J$  is obtained.

The above may be expressed in the form  $JH = I^2Rt \times 10^7 = VIt \times 10^7 = V^2t/R \times 10^7$ . Thus, it will be seen that it is necessary to measure only *two* of the quantities  $V$ ,  $I$ ,  $R$ , in order to obtain an equation for  $J$ , and therefore a choice of three methods is available.

The electrical method consists in heating a given mass of water through a known range of temperature by immersing in it a wire heated by an electric current, and measuring the heat energy communicated to the water in terms of electrical units. *Joule* tried this method, but it was regarded by him as less trustworthy than the direct methods described above.

*Griffiths*, however, carried out a series of very careful determinations, in which a platinum wire was coiled inside a calorimeter containing water, the calorimeter being suspended in a constant temperature enclosure. The wire was heated by a current from storage cells, and the quantities  $V$  and  $R$  were measured. The temperatures were measured by an accurate mercury thermometer which had been standardised by comparison with a gas thermometer. The method gave  $4.194 \times 10^7$  ergs as the mean value of  $J$  at  $15^\circ\text{C}$ .

*Schuster* and *Gannon* also made a determination by a similar method, measuring the work done in terms of  $V$ ,  $I$ , and  $t$ . Errors were minimised by making the experiments of short duration, using a small rise of temperature, about  $2^\circ\text{C}$ . The mean result obtained was  $4.191 \times 10^7$  ergs at  $19^\circ\text{C}$ .

*Callendar* and *Barnes* also adopted the method depending on the measurement of  $V$  and  $I$ , using the continuous flow electric calorimeter (page 122). The difference of temperature between the inflowing and the outflowing water was measured by platinum thermometers, probably correct to  $0.001^\circ\text{C}$ . The final result obtained was given as  $4.184 \times 10^7$  ergs at  $15^\circ\text{C}$ .

## 9. Joule's Experiments on the Compression and Expansion of Gases

(1) PRELIMINARY NOTE ON WORK DONE BY PRESSURE.—Consider a piston in a cylinder separating two quantities of gas at different pressures. The result will be that the piston will be driven by the high pressure gas towards the low pressure gas. It is required now to find how the work done by the gas depends on the pressures of the two quantities of gas, the area,  $A$ , of the face of the piston and the distance,  $l$ , the piston moves.

Let the gas pressures be  $P + p$  and  $p$  respectively, the higher pressure being on the left of the piston,  $R$  (Fig. 149), and suppose that the pressures remain constant as the piston moves. Then the force exerted by the high pressure gas on the left face of the piston is  $(P + p)A$ , and the force exerted by the low pressure gas on the right face of the piston is  $pA$ . The resultant force is therefore  $PA$  directed from left to right. The work done by this force in moving the piston is  $PA \cdot l = P \cdot Al$ . Now,  $Al$  is the volume swept out by the piston, therefore the work done is  $P \times \text{Volume swept out by the piston}$ .

If the gas to the right of the piston is air open to the atmosphere,  $p$  is equal to the atmospheric pressure, and  $P$  is therefore the pressure of the gas to the left

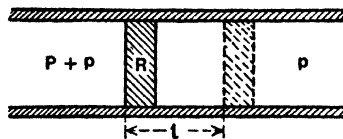


FIG. 149.

of the piston in excess of the atmospheric pressure. This excess pressure is often called *the* pressure of the gas, and the above deduction may be expressed:—"If a piston is moved along a cylinder by the action of a gas at constant pressure, the work done by the gas is measured by the product of the pressure of the gas and the volume swept out by the piston."

(2) JOULE'S EXPERIMENTS ON GASES.—When a gas is compressed, the work done on it in effecting the compression produces heat, which raises the temperature of the gas. Similarly, when a gas expands, it does work against the external pressure and consequently there is an absorption of heat, which lowers the temperature of the gas (see page 226 (g), (h)). It cannot be assumed, however, that *all* the work spent in compressing a gas is converted into heat, or that the heat absorbed during the expansion of a gas is equivalent to the work done. For example, when a steel spring is compressed, nearly all the work done in effecting the compression is spent in giving the spring potential energy, a small fraction only being

spent in heating the steel. Similarly, when a gas is compressed, the work done in compression may be spent partly in imparting potential energy to the gas, and partly in the production of heat.

Joule had reason to believe that in some gases all the work done in compression or expansion had its equivalent in the accompanying thermal effects. This assumption was verified by the following experiment:—If a gas is allowed to expand into a vacuum, *no* external work is done; and, if any internal work is done—that is, if the potential energy of the gas is changed by the expansion—then an equivalent amount of heat will be absorbed, and the temperature of the gas will be lowered. Accordingly, Joule took two reservoirs, H, H' (Fig. 150), communicating by a tube fitted with a stopcock, S. The reservoir, H, contained air under a pressure of 22 atmospheres, H' being completely exhausted of air.

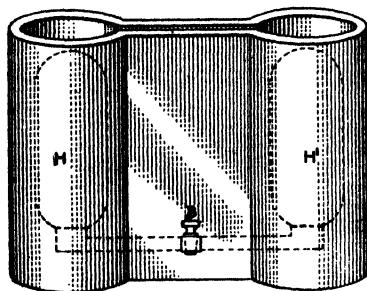


FIG. 150.

These reservoirs were immersed in a large vessel, so constructed that a small quantity of water sufficed to cover them. The temperature of the water was taken, and the stopcock opened. The gas in H suddenly expanded into H'; but after stirring no change in the temperature of the water as a whole could be detected, thus showing that very little or no internal work was done.

Later experiments by Joule and Kelvin on this subject (page 288) showed that when a gas expands without doing external work, a *slight absorption of heat* takes place, which is smaller the more nearly the gas conforms to Boyle's law, and would be zero for a perfect gas conforming exactly to that law. Thus, assuming that, for air, the external work done during expansion is equivalent to the heat absorbed, it is evident that this fact may be adapted readily to the experimental determination of the equivalence of heat and work.

Joule adopted this method: In one of his experiments, a reservoir containing air under a pressure of 22 atmospheres, and immersed in water contained in a large calorimeter, was employed. The air escaped from the reservoir through a stopcock constructed to regulate the velocity of its flow, and through a long coil of lead

tubing, to the exterior where it was collected in a large vessel under the pressure of the atmosphere. The stopcock and tubing were immersed in the calorimeter, so that the air arrived at the exterior at the temperature of the calorimeter, and without any appreciable velocity. Had the air been allowed to expand freely into the atmosphere, it would have carried away energy in the form of kinetic energy, and thus the fall of temperature would have indicated a greater absorption of heat than that equivalent to the external work done. The temperature of the water in the calorimeter was taken before and after the expansion; from the fall of temperature and the water equivalent of the calorimetric apparatus the heat,  $H$ , absorbed by the expansion of the air was calculated.

To determine the work,  $W$ , to which this is equivalent, it was necessary to calculate the external work done by the gas during its expansion. Now the gas expanded against the pressure of the atmosphere, which is constant during an experiment of short duration; hence, the work,  $W$ , done by the gas is equal to the product of the atmospheric pressure,  $P$ , and the volume,  $V$ , of the air collected after escaping from the reservoir and measured at atmospheric pressure (see page 237). Thus:—

$$W = PV, \quad \text{and} \quad \frac{W}{H} = J.$$

From several experiments, of which the one described above is one of the simplest, Joule deduced results which agreed closely with those obtained previously by frictional methods.

## 10. Conservation of Energy

As mentioned in Art. 1, it has been proved that whenever energy in one form disappears, it is always replaced by an exactly equivalent amount of other forms of energy. Hence, when all the forms of energy are taken into consideration—

(1) *The total amount of energy in the universe is absolutely unalterable; that is, no energy is ever created or destroyed.*

(2) *The various forms of energy may be converted one into another, though not always at will.*

Energy may thus be transferred from one body to another, or transmuted from one kind to another, but the energy lost by one body is gained by other bodies, and *vice versa*. The principle

contained in the above propositions is known as the **conservation of energy**.

In nearly all operations some energy is wasted in friction, etc., going into the form of heat energy; as a rule very little of this energy is recoverable by human agency, and therefore it is said to be *dissipated*. In any store of energy, that portion which can be used for actual mechanical work is spoken of as the *available* energy.

## 11. The First Law of Thermo-Dynamics

This law asserts the equivalence of heat and work in a definite ratio determined by experiment. It may be stated thus:—**When work is transformed into heat, the quantity of heat produced is equivalent to the quantity of work expended in its production; and conversely, when heat is transformed into work, the quantity of work produced is equivalent to the quantity of heat expended in its production.** In both cases,

$$W = JH,$$

where  $W$  denotes any definite quantity of work,  $H$  the equivalent quantity of heat, and  $J$  the ratio of these two quantities. This ratio is known as **Joule's equivalent**, or the **mechanical equivalent of heat**, or the *specific heat of water in mechanical units*.

The latest figures for the value of  $J$  in the different systems of units are given below:—

778 foot-pounds per water-pound-degree Fahrenheit.

1400 foot-pounds per water-pound-degree Centigrade.

0.427 kilogram-metre, or 427 gram-metres per water-gram-degree Centigrade.

$4.19 \times 10^7$  ergs per water-gram-degree Centigrade, or calorie.

4.19 joules per water-gram-degree Centigrade, or calorie, since  $10^7$  ergs is called a *joule*.

## 12. Calculation of $J$ from the Two Specific Heats of a Gas

Reference has been made already (page 124) to the fact that the specific heat of a gas at constant pressure is greater than that at constant volume. This is evidently due to the fact that when a gas is heated at constant pressure it expands, and part of the heat absorbed is expended in doing external work, the *remainder* being spent in raising the temperature of the gas. When, however, a gas is heated at constant volume, *no* external work is done, and *all* the heat absorbed is spent in raising the temperature of the gas.

From this it appears that, since almost no internal work is done (Art. 9), the difference between the two specific heats should be equivalent to the external work done during the expansion, at constant pressure, of one gramme of the gas for one degree rise in temperature. Thus:—

If  $s_p$  = the specific heat at constant pressure,

$s_v$  = the specific heat at constant volume,

$w$  = the work done during the expansion of 1 grm. of gas per  $1^\circ$  C. rise in temperature,

$h$  the heat equivalent of this work;

$$\therefore s_p - s_v = h = \frac{w}{J}.$$

And if  $s_p$ ,  $s_v$ , and  $w$  are known,  $J$  can be calculated.

In the case of air *Regnault* was the first to determine  $s_p$ , the value obtained being 0.2374 (page 124). A later and probably more correct value of  $s_p$  is 0.2410 at  $20^\circ$  C. *Joly* was the first to determine  $s_v$ , the value obtained being 0.1715 (page 175). Taking the values 0.2410 and 0.1715, it follows that  $h = 0.0695$ .

To calculate  $w$ , the increase of volume of 1 grm. of air per  $1^\circ$  C. rise of temperature and the pressure at which this occurs must be known. Take the pressure as 76 cm. of mercury at  $0^\circ$  C. In absolute units this is  $76 \times 13.6 \times 981$ , or  $1.014 \times 10^6$  dynes per cm.<sup>2</sup> Also, at  $0^\circ$  C. and a pressure of 76 cm. of mercury, 1 litre of air weighs 1.293 grm. Hence, the volume of 1 grm. of air at this temperature and pressure is  $\frac{1000}{1.293} = 773$  c.c., and the increase of volume for  $1^\circ$  C. rise of temperature is  $\frac{773}{273} = 2.83$  c.c. Hence,

$$w = 1.014 \times 10^6 \times 2.83 \text{ ergs};$$

$$\therefore J = \frac{1.014 \times 2.83}{0.0695} \times 10^6 = 4.18 \times 10^7 \text{ ergs per calorie.}$$

The first calculation of this nature was made by *Mayer* in 1842. Owing to inaccurate data, the value of  $J$  obtained was far from the truth.

The difference between the two specific heats,  $s_p$  and  $s_v$ , per given volume is the same for all perfect gases. It will be seen that if the values of  $J$  and  $s_p$  are known, the value of  $s_v$  can be obtained from the relation given above.

### 13. Laboratory Determinations of the Value of J

Several methods for the determination of the value of the mechanical equivalent of heat are available as laboratory experiments and will be described:—

(1) SIMPLE LABORATORY METHOD.—The first method is a simple one depending upon the heat produced by allowing a body of known mass to fall freely through a measured distance and noting the change of temperature.

*Experiment.* Obtain a cardboard tube about 2 m. long and 5 cm. in diameter, and two corks which fit the tube tightly. Take about 500 grm. of small lead shot, place in a dish and insert a thermometer. Allow the shot to acquire the temperature of the room and read this temperature. Then pour the shot into the tube, close the tube and hold it vertical. Quickly invert the tube so that the shot fall the whole length of the tube. Repeat the operation 100 times, making sure that the shot fall the whole length of the tube each time. Remove one cork from the tube, pour the shot into the dish and again take their temperature as soon as possible. From the change of temperature, calculate the heat developed:—

Let  $m$  = mass in grm. of the shot,  $s$  = specific heat of lead,  $t$  = change of temperature in degrees C. Then:—

$$\text{Heat gained by lead} = mst \text{ calories.}$$

Let  $h$  = distance in cm. the shot fall each time,  $n$  = number of times the tube is inverted. Then:—

$$\text{Work done by gravity} = nmh \text{ grm. cm.} = nmhg \text{ ergs;}$$

$$\therefore J = \frac{nmhg}{mst} = \frac{nhg}{st} \text{ ergs per calorie.}$$

The results obtained by this method are not very accurate, owing to several sources of error which will be obvious. More accurate results can be obtained, however, by either of the following methods:—

(2) PULJ'S APPARATUS.—This is a simplified form of the apparatus used by Joule in his later experiments on fluid friction. It comprises two steel or brass cones, the outer one being fixed to a revolving shaft, while the inner one, containing water or mercury, is free to move according to the amount of friction between the two.

The revolving shaft is rotated by a hand wheel and leather belt (Fig. 151), and the number of revolutions is given by a counter attached to the shaft. To the inner cone is attached a wooden disc; a string is fastened round the grooved edge of this disc and then passes over a pulley, carrying a weight at its end. The magnitude of the weight and the speed of rotation are adjusted so that the weight hangs stationary, *i.e.* it is just sufficient to prevent rotation of the inner cone. The inner cone is then in equilibrium under two forces, the frictional force and the tension in the string.

The two cones are weighed, together with a stirrer, and again about three-fourths full of water, the temperature being taken with a mercury thermometer. The rotation is then commenced and

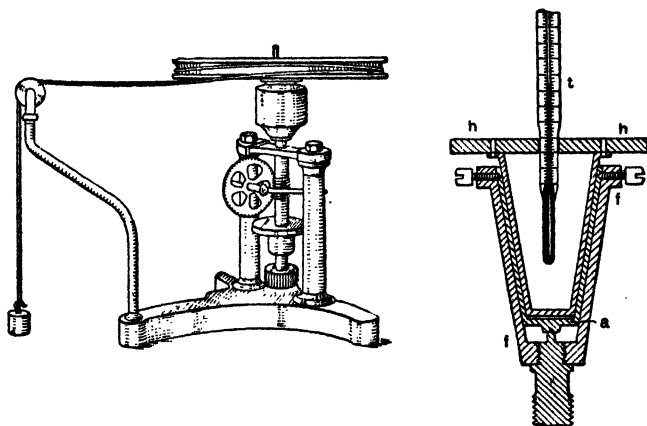


FIG. 151.

continued until a suitable increase of temperature is obtained, the water being well stirred, and the number of revolutions made is observed.

Let  $m$  = mass in grm. of the water,  $w$  = mass in grm. of the cones,  $s$  = specific heat of cones and stirrer, and  $t$  = change of temperature in degrees C. Then:—

$$\text{Heat developed} = (m + sw) t \text{ calories.}$$

Let  $M$  = mass in grm. attached to disc,  $r$  = radius of disc in cm., and  $n$  = number of revolutions. The stretching force in the string,  $Mg$ , applies a moment at the edge of the disc of magnitude  $Mgr$ . This is balanced by the frictional forces which act on the



inner cone. The couple exerted by the frictional forces is therefore  $Mgr$ , and this is also the couple exerted on the shaft by the driving belt. Hence,

$$\text{Work done} = Mgr2\pi n \text{ ergs};$$

$$\therefore J = \frac{2\pi nrMg}{(m + sw)t} \text{ ergs per calorie.}$$

(3) CALLENDAR'S APPARATUS.—In this apparatus, heat is developed by the friction between a silk band and the surface of a revolving drum, containing water, around which it passes, and is

measured by the change in temperature of the drum and its contents.

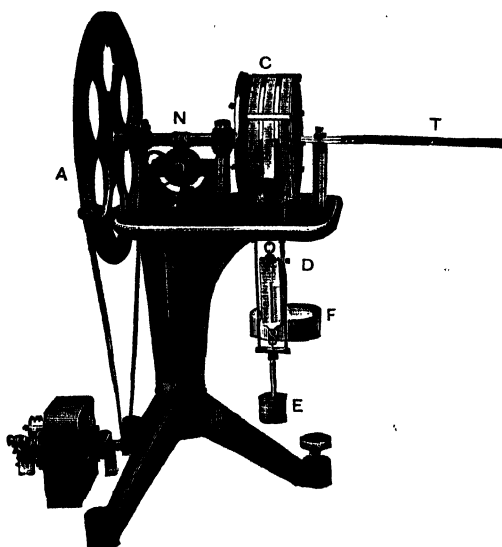


FIG. 152.

The drum, C (Fig. 152), is made of thin brass and mounted so that it can be rotated on a horizontal axis, by a driving wheel, A, driven by hand or by an electric motor. A counter, N, records the number of revolutions made. The silk band passes one and a half times round the drum. For half this distance the band is double, and fixed to one end is a single

band which passes round the drum for the other half of the distance. The double band supports a large weight, F, and the single band a smaller weight, E. E is supported partly by a spring balance, D, attached to the frame of the apparatus. A weighed quantity of water, nearly filling the lower half, is placed in the drum, and the temperature is read by a thermometer, T, bent so that the bulb is immersed in the water, the stem passing through an axial hole in the side of the drum. The surface of the drum is smooth and bright, and the silk band should be clean and dry.

When the drum is rotated, the friction causes  $F$  to rise and the weights,  $F$  and  $E$ , are adjusted so that they remain in floating equilibrium. Any variation in the friction is eliminated to a great extent by the action of the spring balance,  $D$ . If, for example, the friction becomes less,  $F$  tends to fall and  $E$  to rise, a smaller proportion of the weight  $E$  being taken by  $D$  and more by the belt. This increased tension of the belt thus increases the friction again and restores the original balance. The rotation is continued at a rate of about 100 revolutions per minute until a change of temperature of about  $5^{\circ}\text{C}$ . has been obtained.

As in the previous method, the heat developed is given by the expression

$$\text{Heat} = (m + sw) t \text{ calories,}$$

where  $m$  is the mass in grm. of the water,  $w$  the mass in grm. of the drum,  $s$  its specific heat, and  $t$  the change of temperature in degrees C.

If  $M_1$  = mass in grm. of  $F$ ,  $M_2$  = mass in grm. of  $E$ ,  $S$  = reading in grm. of spring balance, the effective tension in the silk band is  $(M_1 - M_2 + S)$  grm. weight. And if  $r$  = radius of drum in cm., and  $n$  = number of revolutions, the work done is given by:—

$$\text{Work done} = 2\pi nr (M_1 - M_2 + S) g \text{ ergs;}$$

$$\therefore J = \frac{2\pi nr (M_1 - M_2 + S) g}{(m + sw) t} \text{ ergs per calorie.}$$

(4) JOULE'S CALORIMETER.—This method involves the use of a calorimeter to measure the heat, in calories, produced by the passage of an electric current through a wire, and depends upon Joule's law (Art. 8), the electrical energy being obtained from observation of any two of the quantities  $V$ ,  $I$ ,  $R$ , involved. In the method usually carried out in the laboratory, the quantities  $V$  and  $I$  are determined with a voltmeter and ammeter respectively.

A length of thin manganin wire, varnished with shellac, is wound into a spiral. Manganin is used because its resistance does not alter appreciably with temperature. The ends of the spiral are connected by short thick copper wires to two terminals fixed in a disc of wood which fits as a lid into a copper calorimeter. The resistance of the wire is about 3 ohms. Two holes are bored in the disc through which may be passed a thermometer,  $T$ , graduated in tenths of a degree, and a stirrer,  $S$  (Fig. 153). The calorimeter is enclosed in the usual way in a larger vessel. The current is obtained from a battery of storage cells,  $E$ , and an adjustable

resistance, A.R., is included in the circuit so that the current may be kept constant at any desired value. The circuit may be completed or broken by a key, K, and the required electrical quantities are obtained from the ammeter, A, and voltmeter, V.

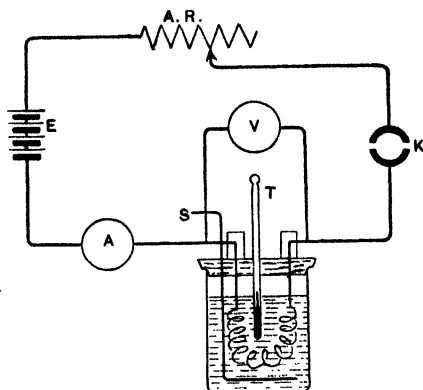


FIG. 153

To make a determination, a known mass of distilled water, enough to cover the spiral of wire, is introduced into the calorimeter, and the temperature of the water is taken. A constant current is allowed to pass for a known time, the water in the calorimeter being well stirred, while simultaneous readings of the ammeter and voltmeter are made. The

final temperature of the water is obtained, after a suitable rise has occurred, usually about  $6^{\circ}\text{C}$ .

If  $m$  grm. is the mass of the water,  $w$  grm. that of the calorimeter,  $s$  the specific heat of the calorimeter, and  $t^{\circ}\text{C}$ . the rise of temperature, then the heat developed is given by

$$\text{Heat} = (m + sw) t \text{ calories.}$$

If  $V$  volts and  $I$  amperes are the readings of the voltmeter and ammeter respectively, and  $T$  seconds is the time of the experiment, then the energy expended is

$$\text{Energy} = VIT \times 10^7 \text{ ergs;}$$

$$\therefore J = \frac{VIT \times 10^7}{(m + sw) t} \text{ ergs per calorie.}$$

**Example.**—A steady current of 1.66 amperes was passed through a coil of wire of resistance 15 ohms immersed in water in a calorimeter. The total water equivalent of the calorimeter and its contents was 240 grm., and in 120 sec. the temperature was raised by exactly  $5^{\circ}\text{C}$ . Find the mechanical equivalent of heat.

$$\text{Heat developed by the current} = I^2 R t \times 10^7,$$

$$= 1.66^2 \times 15 \times 120 \times 10^7 \text{ ergs.}$$

$$\text{Heat absorbed by water and calorimeter} = 240 \times 5 \text{ calories;}$$

$$\therefore J = \frac{1.66^2 \times 15 \times 120 \times 10^7}{240 \times 5} = 4.33 \times 10^7 \text{ ergs per calorie.}$$

In the last three methods described, corrections should be made in each case for the loss of heat by radiation in the course of the determination. This may be effected in the manner already described (page 118) in measurements of specific heat.

(5) CONTINUOUS FLOW CALORIMETER.—A simplified form of the continuous flow electric calorimeter devised by *Callendar* (page 122) can be obtained and used in the laboratory for the determination of *J*. In this form of apparatus, a steady flow of water is maintained through a narrow tube in which it is heated by an electric current passing through a spiral of manganin wire. After some time a steady state is reached, and, except for the heat lost by radiation, all the electrical energy is used to heat the water passing through the tube, so that the water equivalent of the apparatus is not required. The correction for the loss of heat by radiation is eliminated by using two different rates of flow of the water and adjusting the supply of electrical energy to give the same temperature change in each case.

The water flows from a Mariotte bottle, *H* (Fig. 154), to the vessel, *K*, which is used to maintain a constant flow, surplus water overflowing down the central tube. The water passes from *K* to the jacket of the calorimeter, *C*, and then enters the central tube in which it is heated, always entering the calorimeter at the temperature of the jacket. The temperatures of the water on entering

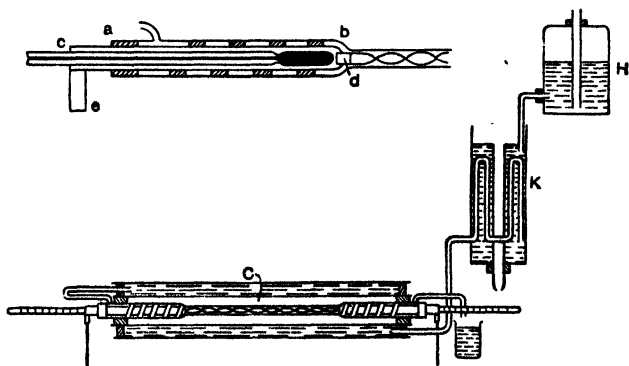


FIG. 154.

and leaving the calorimeter are measured by means of mercury thermometers, graduated in tenths of a degree, placed in the wide ends, *ab*, of the calorimeter tube. A spiral strip of metal ensures

that the water flows round the thermometer in each case. The electric current is supplied by a battery of storage cells, the quantities  $I$  and  $V$  being observed by means of an ammeter and a voltmeter, as described in the previous method above. The rate of flow of the water is found by weighing the quantity collected in a beaker in a known period of time, after the temperatures have become steady. To increase the rate of flow of the water, in order to eliminate the radiation correction, the vessel,  $K$ , is raised and the values of  $I$  and  $V$  adjusted so that the increase of temperature is the same as before. The calculation of the value of  $J$  is effected by using the two sets of observations thus made:—

Let  $m_1$  = mass in grm. of water flowing per second,  $I_1$  = current in amperes,  $V_1$  = potential difference in volts, in the first experiment,  $t$  = change of temperature in degrees C., and  $h$  = loss of heat by radiation per degree change of temperature. Then:—

$$V_1 I_1 = J (m_1 t + ht).$$

Also, if  $m_2$ ,  $I_2$ , and  $V_2$  are the corresponding observations for the second rate of flow, then:—

$$V_2 I_2 = J (m_2 t + ht).$$

From these two equations,  $h$  can be eliminated and  $J$  determined, viz.:—

$$J = \frac{V_1 I_1 - V_2 I_2}{m_1 t - m_2 t}.$$

## CHAPTER XIII

### ISOTHERMALS AND ADIABATICS. CARNOT'S CYCLE. THE SECOND LAW OF THERMODYNAMICS

**BOYLE'S** Law—which deals with the relation between the volume and pressure of a gas when the temperature is kept constant—was dealt with in Chapter VI., and it was stated that when the results of the experimental investigation were plotted graphically the curve so obtained was called an *isothermal curve*.

#### 1. Isothermals

An *isothermal at any temperature* for a given substance may be defined as a curve which represents, for that temperature, the relation between pressure and volume. As usually plotted, the horizontal axis is taken as the axis of volume and the vertical axis as the axis of pressure.

On a pressure-volume diagram, a line parallel to the axis of volume is termed an *isopeistic*, and a line parallel to the axis of pressure as an *isometric* (page 100).

(a) **ISOTHERMALS FOR PERFECT GASES.**—In the case of perfect gases, the relation between pressure and volume at constant pressure is expressed by Boyle's law. Hence, the isothermals for gases which conform to this law are curves which satisfy the relation

$$PV = \text{constant} \text{ (page 83).}$$

A curve satisfying an equation of this type is a *rectangular hyperbola*. The value of the constant will be different at different temperatures; but it has been established that if  $T$  denote the absolute temperature, then

$$\frac{PV}{T} = R,$$

where  $R$  is a constant for the same mass of the same gas.

Hence, if volumes are denoted by abscissae and pressures by the corresponding ordinates, the isothermals for a perfect gas are curves such that for any given value of  $T$  the quantity  $PV/T$  has some constant value. For example, if the volume of the gas is

1 litre at  $0^{\circ}\text{C}$ . and a pressure of 1 atmosphere, then, in the units given,  $P = 1$ ,  $V = 1$ , and  $T = 273^{\circ}\text{A}$ . Thus  $PV/T = 1/273$ ; that is, when  $T = 273^{\circ}\text{A}$ ., then  $PV = 1$ , and the curve satisfying this relation is the isothermal for  $0^{\circ}\text{C}$ .

Similarly, for the same mass of the gas, when  $T = 373^{\circ}\text{A}$ ., we have  $PV/373 = 1/273$ , or  $PV = 373/273$ , and the curve satisfying this relation is the isothermal at  $100^{\circ}\text{C}$ .

To plot these curves, take convenient values of  $P$  and calculate the corresponding values of  $V$ . Convenient numbers from which to plot the isothermals at  $0^{\circ}\text{C}$ . and  $100^{\circ}\text{C}$ . are shown in the table,

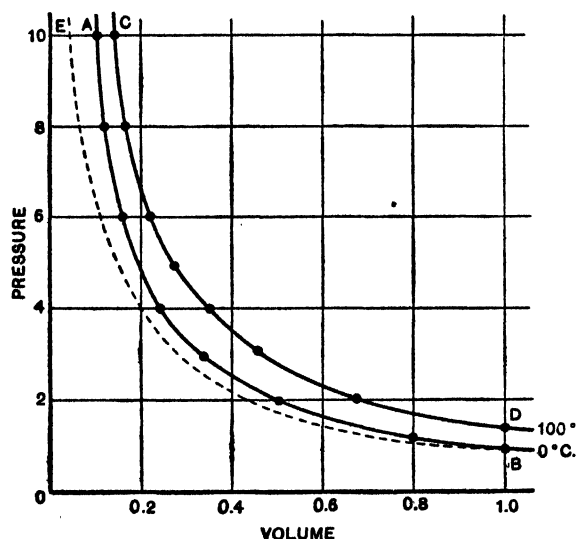


FIG. 155.

At $0^{\circ}\text{C}$ .	
P	V
10	1
8	.125
6	.167
5	.2
4	.25
3	.333
2	.5
1.25	.8
1	1

At $100^{\circ}\text{C}$ .	
P	V
10	.1367
8	.171
6	.228
5	.273
4	.342
3	.456
2	.683
1.367	1

and the curves themselves, AB and CD (Fig. 155), the abscissae representing the volumes, and the ordinates representing the pressures. In this way the isothermals for a series of temperatures may be drawn, each curve representing the relation between pressure and volume at the temperature for which it is drawn.

(b) ISOTHERMALS FOR GASES WHICH ARE NOT "PERFECT."—In the case of a gas which conforms only approximately to Boyle's law, the general character of the isothermals is similar to those for a perfect gas; but in such a case the value of  $PV$  generally decreases as  $P$  increases, and thus the curve becomes less steep as  $P$  increases,

and therefore falls below the true position of the theoretical curve. The dotted line, BE (Fig. 155), represents generally the nature of this departure from the true form of the curve. When a gas approaches its point of liquefaction, the decrease in PV becomes more marked, and the isothermal falls considerably below its theoretical position.

(c) ISOTHERMALS FOR LIQUIDS AND SOLIDS.—The isothermals for liquids and solids are of little interest, for in these cases the volume changes very little for very wide changes of pressure. Hence, if, as before,  $V$  is represented by abscissae and  $P$  by ordinates, then the isothermals for a liquid or a solid are almost straight lines very close together and parallel to the pressure axis. They are approximately isometrics (see Fig. 156 and Fig. 157).

(d) ISOTHERMALS FOR VAPOURS.—The isothermals for a vapour, at temperatures at which the passage from vapour to liquid comes within the limits of the curves, will be considered. Taking the case of aqueous vapour at  $100^{\circ}\text{C.}$ , for pressures less than one atmosphere the isothermal,  $ab$  (Fig. 156) is similar to that of a gas; but, as explained above, it falls considerably below the position demanded by Boyle's law. At a pressure of one atmosphere condensation commences, and a considerable change of volume is effected at constant pressure; this part of the isothermal,  $bc$ , therefore is horizontal or parallel to the volume axis. When the vapour is converted completely into water, the isothermal,  $cd$ , assumes the form characteristic of a liquid—that is, it passes upwards in a direction almost parallel to the pressure axis. Actually this portion of the isothermal would be so close to the pressure axis as to be almost coincident with it. For the sake of clearness, however, the complete curve is shown. In the portion,  $ab$ , of this isothermal the substance exists as vapour, in  $bc$  as both vapour and liquid, and in  $cd$  as liquid only. The relative quantities of vapour and liquid present in conditions corresponding to the position of any point,  $e$ , on  $bc$  is determined by the ratio  $be : ec$ .

Now consider the isothermal for  $130^{\circ}\text{C.}$  The general course of the curve is similar to that at  $100^{\circ}\text{C.}$ , but condensation does not take place until a pressure of about 2.7 atmospheres is reached. For this reason the volume of steam when condensation occurs is much less than at  $100^{\circ}\text{C.}$  On the other hand, the volume of water produced is greater than at  $100^{\circ}\text{C.}$ , for the expansion due to the increase of temperature more than counterbalances the compression produced by the increase of pressure.



From this it is evident that the transition from the gaseous to the liquid state becomes less abrupt as the temperature rises. This is indicated by the decrease in length of the horizontal portion of the isothermal. At the point, *b*, the substance is a vapour, at *c* it is a liquid; hence, as *b* and *c* approach one another, the intermediate condition, in which the substance exists both as liquid and as vapour, becomes less marked. This suggests the possibility that at a sufficiently high temperature the points, *b* and *c*, may coincide, and at the point of coincidence the substance may be considered

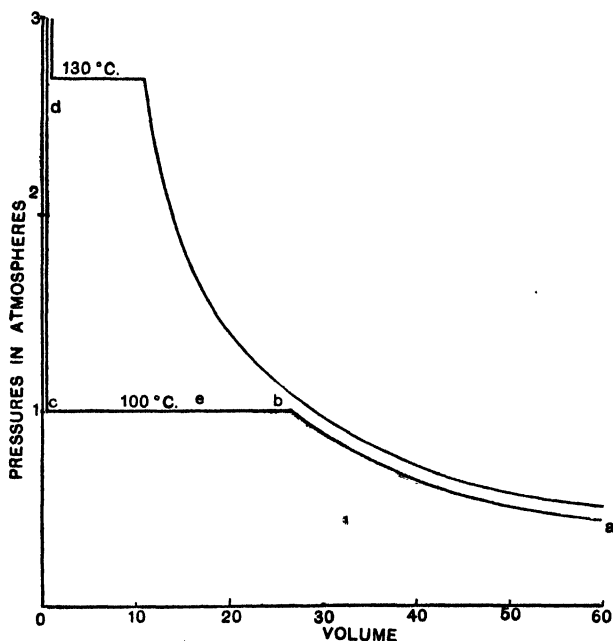


FIG. 156.

either as a vapour or as a liquid—that is, these two conditions may merge into one.

## 2. Andrews' Experiments

The hypothesis mentioned in the last paragraph above was put to the test of experiment by *Andrews* in the case of carbon dioxide, and it was shown to be true. The isothermals for this gas at several different temperatures were determined, and it was found that at  $31^{\circ}\text{C}$ . the horizontal part of the curve disappeared, the

point which represented it corresponding to a pressure of 74 atmospheres. This point was called the critical point, which may

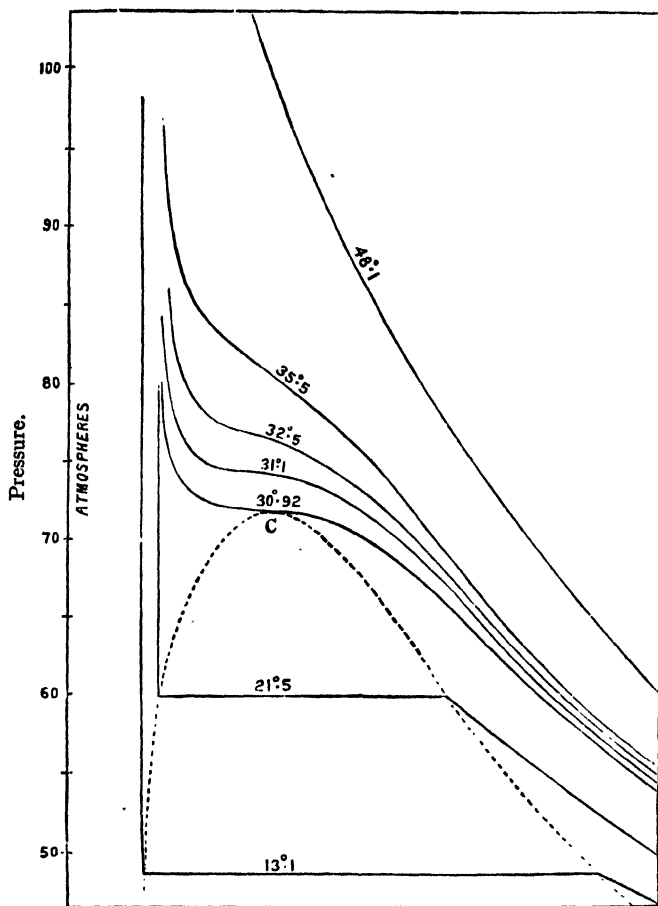


FIG. 157. Volume.

Isothermals for Carbon Dioxide at different temperatures (Andrews').

be defined generally as the particular conditions of temperature and pressure which determine, for any substance, the coalescence or continuity of the gaseous and liquid states.

The condition of the substance corresponding to the critical point is sometimes referred to as the **critical state** of the substance. The **critical temperature** for any substance is the temperature at which, for a given pressure, the substance passes through the critical state. The critical temperature for carbon dioxide is therefore about  $31^{\circ}\text{C}$ .

These facts are represented graphically for the case of carbon dioxide by the curves shown (Fig. 157). The isothermals for temperatures below the critical temperature are of the character described above for aqueous vapour (Art. 1). At the critical temperature the horizontal portion of the curve vanishes at the

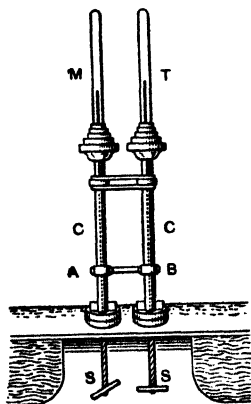


FIG. 158.

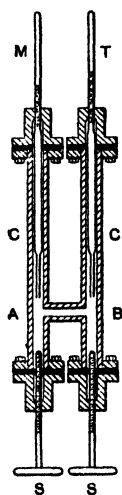


FIG. 159.

point, C, which represents the critical point. For temperatures above the critical temperature the isothermals show at first a double inflection above the critical point, but as the temperature rises the characteristics of the gaseous state are assumed gradually.

The dotted curve shown represents, in its right branch, the locus of points at which condensation commences, and, in its left branch, the locus of points at which condensation is complete.

The right branch therefore marks the left boundary of the entirely gaseous state, and hence is called the **vapour line**. The left branch marks the right boundary of the entirely liquid state, and is called the **liquid line**. These boundaries meet at C, and are continued thence, in an upward direction, by the isothermal for the critical temperature. Within the space bounded by the vapour and liquid lines, the substance exists partly as vapour and partly as liquid.

The data for the construction of these isothermals were obtained by enclosing the gas in a strong capillary tube and subjecting it to hydrostatic pressure. The pressure was indicated by means of an air manometer, the volume by graduations on the capillary tube,

and the temperature was regulated by surrounding the tube with a jacket carrying a stream of water at the required temperature. A general view of Andrews' apparatus is shown (Fig. 158 and Fig. 159). The glass tube, T, contains the gas under experiment, and M is a similar tube containing air which acts as a compressed air manometer for the measurement of the pressure exerted in T. The tubes were secured by water-tight fittings into the metal tubes, CC, which communicate by the cross-tube, AB, and carry the screw plungers, SS, fitted water-tight through the bottom of each tube. The lower parts of the glass tubes, T and M, contained mercury and the rest of the interiors of the glass and metal tubes was filled with water. The pressure was adjusted by means of either of the screw plungers, SS, and the temperature of the substance in T was controlled by surrounding the tubes with a liquid at the required temperature.

### 3. Cagniard de la Tour's Experiments

The critical temperature and pressure for a liquid may be determined also by finding the point at which the maximum vapour pressure curve for the substance ends. If a quantity of a liquid is heated under proper conditions in a closed tube and the pressure is measured, the pressure at any temperature up to the critical temperature is the maximum vapour pressure for that temperature, but beyond the critical temperature the magnitude of the pressure is found to depend upon the quantity of substance present.

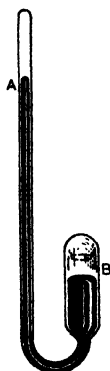


FIG. 160.

In an experiment due to *Cagniard de la Tour*, the liquid at B in the tube, AB (Fig. 160), was heated, and the pressure indicated by the compression of air at A, which was separated from the liquid at B by the mercury in the U-tube. As the temperature rose the surface of separation between the liquid and vapour at B was observed to become less distinct, and at a certain temperature it ceased to exist. This temperature is close to the critical temperature, but the substance is not necessarily in the critical state,

It is evident that, in an experiment of this kind, where the volume occupied by the substance is fixed within narrow limits and cannot be adjusted, as in Andrews' experiments, it is impossible to place in the tube the exact quantity of substance which will, at the critical temperature, give the critical state. If the volume available

in the tube at the critical temperature is greater than the critical volume for the mass of substance taken, then the substance will fill the space as unsaturated vapour, and, in this case, it is possible that the liquid may persist in a superheated state beyond the temperature at which saturation ceases, and then suddenly vaporise at a temperature close to the critical temperature where the surface tension of the liquid reaches its zero value. If, on the other hand, the volume available in the tube is less than the critical volume, then, before reaching the critical temperature, the liquid will fill the space, and, if heated past the critical temperature, it will change, at that temperature, to the gaseous state without any apparent change of state.

These changes, which take place when a liquid is heated in a closed space of *constant*, or nearly constant, volume may be followed by tracing the state of the substance along constant volume lines drawn parallel to the pressure axis (Fig. 157). There is evidently only one line of constant volume which passes through the critical point.

The phenomena of the critical state may be observed and the critical temperature determined by using specially prepared tubes—"Boyle tubes"—containing suitable liquids, such as ether, sulphur dioxide, etc. Such tubes are about 8 cm. in length, 5 mm. internal diameter, with walls about 1 mm. thick (Fig. 161) to give the necessary strength. The tube is sealed after heating the liquid to its normal boiling point, so that it contains only the liquid and its vapour, the former occupying about half the volume.

The tube is suspended side by side with a sensitive thermometer of suitable range in a bath of glycerin, or oil; or it may be heated by means of a small electric furnace which has the advantage that the temperature may be controlled more easily. As there is some danger of the bursting of the tube, observations should be made through a sheet of plate glass for safety. If a bath of glycerin, or oil, is used, the temperature should be kept uniform by vigorous stirring from time to time.

In the case of sulphur dioxide, with a tube about half full of liquid, the liquid slowly expands up to about  $150^{\circ}\text{C.}$ , and then rapidly expands up to within 1 cm. of the end of the tube. The meniscus then becomes flat and suddenly disappears, the whole



FIG. 161.

mass of the substance being now in a homogeneous state. The temperature is then observed. On allowing to cool, the meniscus suddenly reappears much nearer the end of the tube, and then sinks rapidly as cooling proceeds. The temperature is again observed when the meniscus reappears. The mean temperature may be taken as a value of the critical temperature.

#### 4. Deviation From Boyle's Law

Experiments were made in 1827 by Despretz in which he found that most gases more or less disobeyed Boyle's law. In testing the truth of Boyle's law, the interest and importance of the experiments depend upon the accurate measurement of the small deviations from the law which are exhibited by ordinary gases. Hence, very accurate measurements are required, and the ordinary method of experiment fails in that when the pressure is very great the volume of the gas is very small, and difficulty is experienced in measuring it accurately.

The first *accurate* experiments were made by Regnault, the apparatus consisting of a U-tube. The upper end of the short limb containing the gas under experiment could be connected with or cut off from a reservoir of the compressed gas, at will. The pressure was varied by forcing in mercury at the bottom of the U-tube. The short limb was divided into two equal volumes, and the first experiment consisted in beginning with the gas at one atmosphere pressure, and then increasing the pressure until the volume was halved. If it required exactly two atmospheres to halve the volume, Boyle's law was true within these limits of pressure. Gas was then allowed to enter the short limb from the reservoir until the original volume was attained and the experiment was repeated, the lower pressure being now about two atmospheres and the higher pressure about four atmospheres. In this way the law was tested by successive steps in each of which the lower pressure was nearly equal to the higher pressure in the previous. In all cases the volume occupied by the gas operated upon was the same initially.

The total length of the mercury column at the highest pressure was 80 ft., the lower 40 ft. being inside a tower, the remainder supported by a scaffold. The height of the mercury column was measured by a cathetometer carried on a lift in the tower, but outside the tower the tubes were graduated in mm. and the readings taken directly. Allowances were made for temperature

variations, compression of the mercury under its own pressure, and expansion of the glass tube by the internal pressure.

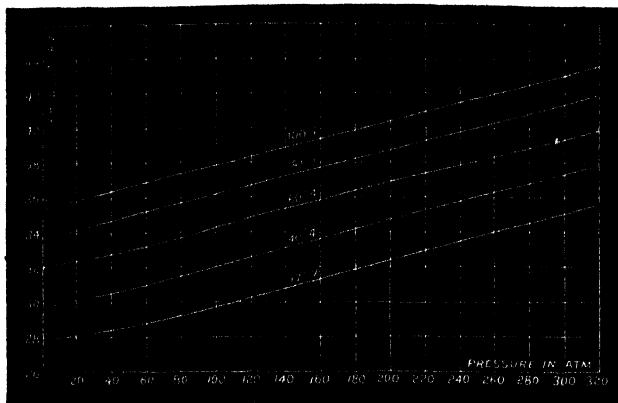


FIG. 162.

Modified Isotherms for Hydrogen (Amagat).

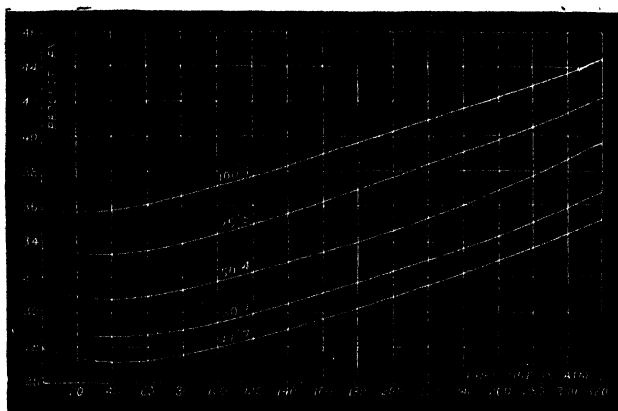


FIG. 163.

Modified Isotherms for Nitrogen (Amagat).

Regnault found that no gas obeyed Boyle's law exactly, though in the case of what were then called permanent gases—gases not liquefiable by methods then available—the departure from Boyle's

law was very small. In the case of the more easily liquefiable gases such as carbon dioxide the deviation was very considerable. In most cases the product,  $PV$ , became smaller and smaller as  $P$  increased. The only exception to this found by Regnault was hydrogen, in which case the product,  $PV$ , became larger, though this result must be modified in the light of later experiments.

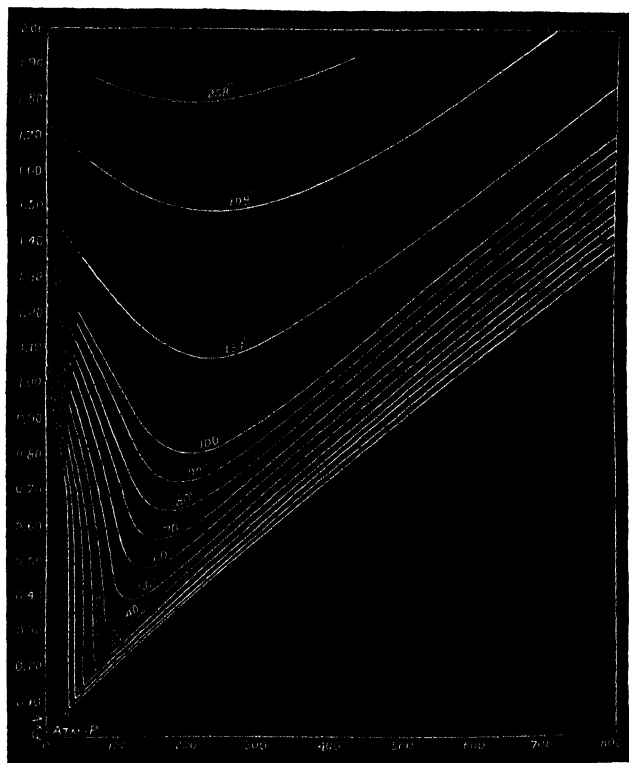


FIG. 164.

Modified Isothermals for Carbon Dioxide (Amagat).

The meaning of the decrease of  $PV$  in the case of carbon dioxide is that the gas is more compressible than Boyle's law allows; the increase in the case of hydrogen shows that this gas is less compressible.

The next set of experiments were made by Natterer during his research on the liquefaction of oxygen, hydrogen, and air. It was



found that for oxygen and air the decrease in the value of  $PV$  with increase of  $P$  did not continue indefinitely, but attained a minimum at a certain pressure, and beyond this limit the value of  $PV$  increased with increase of  $P$ , as in the case of hydrogen.

A thorough investigation of the question was commenced by Amagat in 1870. A long steel tube, placed down the shaft of a mine 1000 ft. deep, was used to contain the mercury. Pressures up to 400 atmospheres were attained. The results of the experiments showed clearly that for all gases the value of  $PV$  first decreases with  $P$ , attains a minimum, and then increases as  $P$  increases. In the case of any given gas the fall of  $PV$  to a minimum, and the subsequent rise, is more marked the nearer the temperature of the gas is to its critical temperature; and it is probable that at temperatures sufficiently high above the critical temperature the value of  $PV$  would show only an increase with  $P$ .

The case of hydrogen illustrates this. At ordinary temperatures hydrogen is further removed from its critical temperature than any other gas except helium; and, as far as experiments go, the value of  $PV$  increases with  $P$ . If in the case of hydrogen at ordinary temperatures the value of  $PV$  does pass through a minimum, the range of pressure through which  $PV$  decreases is very short, and the minimum is attained at a very low pressure. No trustworthy observations have yet been made as to the deviations of hydrogen from Boyle's law at very low pressures. Rayleigh has shown, however, that oxygen and some other gases obey Boyle's law accurately for low pressures of the order of 1 mm. of mercury. If experiments were made with hydrogen at very low temperatures it would probably be found to behave exactly like other gases, and the fall to the minimum, and subsequent rise, of  $PV$  would be more and more marked the lower the temperature.

Amagat's results are best indicated by curves showing for different gases how  $PV$  varies with pressure. If abscissae represent pressures, and ordinates the corresponding values of  $PV$ , then, in the case of a gas which conforms strictly to Boyle's law, the curve showing the relation between  $PV$  and  $P$  would be a straight line parallel to the pressure axis. The nature of the deviations from Boyle's law are shown clearly for hydrogen (Fig. 162), nitrogen (Fig. 163), and carbon dioxide (Fig. 164).

In the case of carbon dioxide, the effect of proximity to the critical temperature is brought out clearly. For hydrogen, it will be seen that the minimum, if it occurs at ordinary temperatures, must be looked for at very low pressures.

## 5. Adiabatics

An **adiabatic** is a curve showing the relation between the pressure and volume of a substance under the condition that there is no transfer of heat between the substance and any external body during any changes to which it may be subjected; that is, during an adiabatic change no heat passes directly into or out of the substance.

If, during the change, work is done *on* the substance, say, by compressing it, then part or all of that work may be converted into heat which enters the substance. Or, if work is done *by* the substance, say, in allowing it to expand against external pressure, then the substance loses heat equal to or greater than the heat equivalent of the work done. Hence, adiabatically, a substance can rise in temperature only when work is done *on* it, and fall in temperature only when external work is done *by* it. The amount of heat gained or lost in this way depends upon the changes that take place in the internal energy of the substance; for example, if during a change in which work is done *on* the substance the internal or molecular energy of the substance increases, then only a small quantity of energy, equivalent to the difference between the work done on the substance and the gain in molecular energy, is converted into heat which raises the temperature.

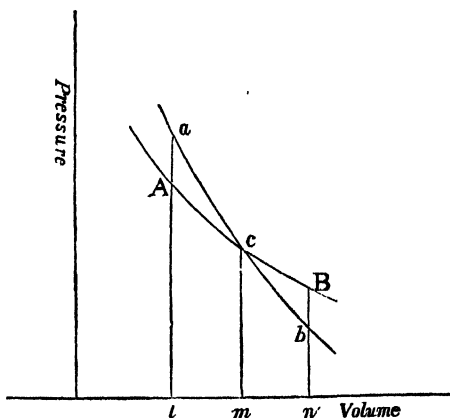


FIG. 165.

It can be shown readily, in a general way, that an adiabatic for any substance must be "steeper" than an isothermal for the same substance. Let *AB* (Fig. 165) represent an isothermal for a given substance, say, air. Then, if the air is compressed *isothermally* from the state represented by *c* to that represented by *A*, the pressure increases from that represented by *mc* to that represented by *lA*. But if, starting from the same point, *c*, the substance is compressed *adiabatically*, then the work done during the compression is, in the case of air, almost all converted into heat which is developed

in the substance; this heat causes a rise of temperature, and consequently, for any given volume during the compression, the corresponding pressure is greater than during the isothermal compression; that is, the adiabatic curve,  $ca$ , runs from  $c$  above the isothermal curve,  $cA$ . Thus, if the same amount of compression is effected in both cases, the pressure increases from the value represented by  $mc$  to that represented by  $lA$  in the isothermal change, and to that represented by  $la$  in the adiabatic change. Similarly, if the substance expands adiabatically from  $c$ , the work done during expansion will cause an abstraction of heat; this will cause a fall of temperature, and consequently, for any given volume during expansion, the corresponding pressure will be less than during isothermal expansion; that is, the adiabatic curve,  $cb$ , lies below the isothermal curve,  $cB$ . Hence, it is seen that the adiabatic curve,  $ab$ , is steeper than the isothermal,  $AB$ .

The divergence between the two curves evidently depends on the energy which appears or disappears as heat during the adiabatic change. In the case of a substance in which all the work done on or by the substance during an adiabatic change is converted, not into heat, but into internal energy—nearly all liquids possess this property—then the cause of the divergence would disappear.

## 6. The Isothermal and Adiabatic Elasticities of a Gas

Elasticity is the general name given to that property of a body by virtue of which it resists, and recovers from, change of shape or volume. All substances resist change of volume—hence what is called **volume elasticity**. It is only solids, however, that have *elasticity of shape*: no fluid—liquid or gas—can offer a permanent resistance to change of shape.

*Volume elasticity is defined as the ratio of the magnitude of the "stress" producing any volume "strain" to the magnitude of the strain produced*, both stress and strain being very small. The *stress* is the change of pressure applied to the fluid, and the *strain* is measured by the ratio of the change of volume to the initial volume—that is, by the change of volume per unit initial volume. Thus, if the initial pressure and volume of a fluid are  $P$  and  $V$ , and if, when the pressure is increased to  $P + p$ , the volume changes to  $V - v$ , both  $p$  and  $v$  being small, the stress is measured by  $p$  and the strain by  $v/V$ . Hence, the modulus of volume elasticity,  $E$ , is given by

$$E = \frac{pV}{v}.$$

The volumes  $V$  and  $v$  are necessarily in the same units, and therefore  $E$  is measured in the same units as  $p$ , so that, if  $p$  is given in dynes per cm.<sup>2</sup>,  $E$  is also expressed in dynes per cm.<sup>2</sup>. Thus if an application of 100 atmospheres pressure to 1 litre of water decreases the volume by 5 c.c., the volume elasticity,  $E$ , of water is given by  $(100 \times 1000)/5$ , i.e. it is  $2 \times 10^4$  atmospheres. In this case although  $p$  is not small,  $v$  is, and the above relation holds.

For any substance the strain may be considered to take place either (1) at constant temperature—that is, under *isothermal conditions*, or (2) without loss or gain of heat to the substance—that is, under *adiabatic conditions*. Hence, the modulus of volume elasticity may be the modulus of isothermal or of adiabatic elasticity, according to the conditions. It follows, from what has been said (Art. 5), that in the case of a gas the modulus of adiabatic elasticity must be greater than the modulus of isothermal elasticity, for when the gas is compressed—that is, strained,—under adiabatic conditions, the heating resulting from the compression tends, by causing expansion, to resist the compression. Thus, the same *stress* will produce a *smaller* strain than is produced under isothermal conditions.

(1) THE ISOTHERMAL ELASTICITY OF A GAS.—To determine the modulus of isothermal elasticity of a gas, let  $P$  and  $V$  denote the pressure and volume of the gas at a given temperature, and let  $P$  and  $V$  be changed *at constant temperature* to  $P + p$  and  $V - v$ , where  $p$  and  $v$  are very small. Then, assuming the gas to be *perfect*, by Boyle's law:—

$$PV = (P + p)(V - v) = PV + pV - Pv - pv;$$

$$\therefore pV - Pv - pv = 0.$$

Since  $p$  and  $v$  are small quantities in comparison with  $P$  and  $V$ , the product  $p v$  is negligible, and thus—

$$pV - Pv = 0;$$

$$\therefore \frac{pV}{v} = P,$$

so that, *the modulus of isothermal elasticity of a perfect gas is measured by its pressure.*

This may be illustrated graphically. Let  $XY$  (Fig. 166) be an isothermal curve, the scales of pressure and volume starting at zero. Supposing that the initial state of the gas is represented by  $A$ , let the

pressure increase slowly, so that any heat developed by the compression may be allowed to escape and the temperature of the gas remain constant, until the state of the gas is represented by B. Join AB and produce it to cut the pressure axis in G. Draw AF and AD perpendicular to the pressure and volume axes respectively, and also BC perpendicular to AF. Then, with the notation used above, for the change represented by AB,

$$p = BC, \quad v = AC, \quad \text{and} \quad V = OD,$$

$$\text{i.e. } \frac{p}{v} = \frac{BC}{AC} = \tan BAC,$$

$$\text{and } \frac{pV}{v} = V \tan BAC = FG.$$

In the limit, when the pressure and volume changes are very small, AG is the tangent to the curve at A, and, since the isothermal curve of a gas obeying Boyle's law is a rectangular hyperbola,  $FG = OF$ . That is, the isothermal elasticity is equal to the pressure.

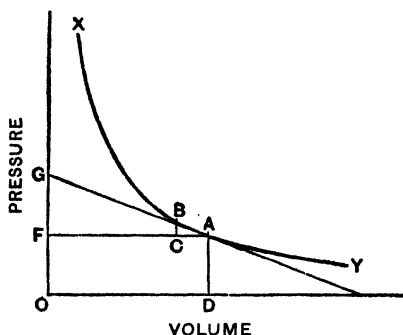


FIG. 166.

(2) THE ADIABATIC ELASTICITY OF A GAS.—The value of the adiabatic elasticity of a gas is not obtained so readily from first principles, but it may be obtained by the following instructive method:—

Consider unit mass of gas. Let  $P$  and  $V$  denote the initial pressure and volume of the gas at absolute temperature,  $T$ . Now let the pressure and volume be changed isothermally to  $P + p$  and  $V - v$ , where  $p$  and  $v$  are very small. The work done on the gas during the change is given by  $Pv$ , and the heat equivalent of this is  $Pv/J$ , where  $J$  is the mechanical equivalent of heat.

If now this heat is given to the gas, the pressure remaining constant at  $P + p$ , the increase of temperature will be  $Pv/Js_p$ , where  $s_p$  is the specific heat at constant pressure. The increase of temperature produces an increase of volume  $\frac{Pv}{Js_p} \cdot \frac{V}{T}$ , since  $\frac{V}{T}$  is the expansion per degree change of temperature at absolute

temperature,  $T$ . The resultant change of volume is therefore:—

$$v - \frac{PV}{Js_p T} v.$$

But  $PV/JT = s_p - s_v$ , where  $s_v$  is the specific heat at constant volume. Hence, the resultant change of volume is:—

$$v - \frac{s_p - s_v}{s_p} v = \frac{s_v}{s_p} v.$$

If the ratio of the specific heats,  $s_p/s_v$ , is denoted by  $\gamma$ , as is usual, then the resultant change of volume is  $v/\gamma$ . The final pressure and volume of the gas are given therefore by  $P + p$  and  $V - v/\gamma$ , and the change of conditions produced is such as would result from a change of pressure from  $P$  to  $P + p$  under adiabatic conditions; for the heat given out during the isothermal change is assumed to be all given back to the gas at constant pressure, and therefore during the total change there is no loss or gain of heat to the substance. Hence

Adiabatic elasticity =

$$\frac{p}{\frac{v}{\gamma}} = \gamma \frac{pV}{v}.$$

But, it was shown above that  $pV/v = P$ , the isothermal elasticity. Therefore, in a perfect gas:—

$$\text{Adiabatic elasticity} = \gamma P.$$

In other words, for a perfect gas,

$$\frac{\text{Adiabatic elasticity}}{\text{Isothermal elasticity}} = \frac{\text{Specific heat of gas at constant pressure}}{\text{Specific heat of gas at constant volume}}.$$

The relation has been proved for a gas. It can be proved that it is universally true. The proof may be illustrated graphically. Let  $RS$  and  $TU$  (Fig. 167) be two isothermals at temperatures,  $t_3$  and  $t_1$ . Take a point,  $A$ , on  $TU$ ; draw a line,  $AB$ , parallel to the pressure axis to cut  $RS$  in  $B$ . Through  $B$  draw a line,  $BC$ , parallel

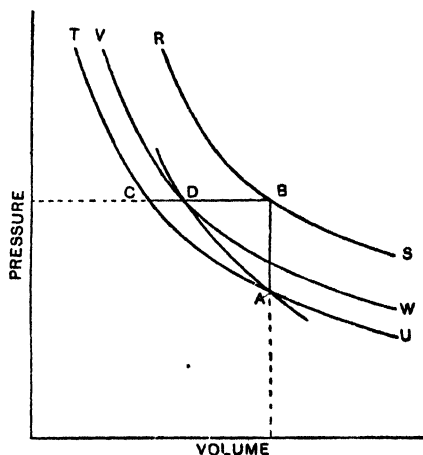


FIG. 167.

to the volume axis to cut TU in C. Through A draw an adiabetic to cut BC in D. Suppose that the isothermal, VW, through D has a temperature  $t_2$ . Now, when a gas changes from the state represented by A to that represented by D, it gains no heat. This is independent of the path by which it changes from A to D. Hence, if it is supposed that AB, BD is the path taken, it follows that the heat gained along AB is equal to the heat lost along BD. Hence,

$$s_v (t_3 - t_1) = s_p (t_3 - t_2).$$

Again, when a gas is heated at constant pressure, the change of volume is proportional to the change of temperature. Thus:—

$$\frac{DB}{CB} = \frac{t_3 - t_2}{t_3 - t_1}, \quad \therefore \frac{CB}{DB} = \frac{s_p}{s_v}.$$

Now CB is the change of volume under isothermal conditions for a change of pressure, AB, and DB is the change of volume under adiabatic conditions for the same change of pressure. Therefore:—

$$\frac{\text{Adiabatic elasticity}}{\text{Isothermal elasticity}} = \frac{CB}{DB} = \frac{s_p}{s_v} = \frac{\text{Sp. heat at const. pressure}}{\text{Sp. heat at const. volume}}.$$

## 7. The Adiabatic Equation

We come now to the relation between pressure and volume when the changes are adiabatic.

It has been shown above that if  $v$  is the change of volume corresponding to a change of pressure,  $P$ , under isothermal conditions, then the change of volume for the same change of pressure under adiabatic conditions is given by  $v/\gamma$ , where  $\gamma$  is the ratio of the specific heats. Or, if  $v$  denote the change of volume under adiabatic conditions,  $\gamma v$  is the change of volume under isothermal conditions. This result may be applied to establish the adiabatic relation between the pressure and volume of a gas. Let the pressure,  $P$ , and volume,  $V$ , of a gas be changed adiabatically to  $P + p$  and  $V - v$ , where  $p$  and  $v$  are very small. Then, if the change from  $P$  to  $P + p$  had taken place isothermally, the volume would have been changed to  $V - \gamma v$ . Hence, by Boyle's law,

$$PV = (P + p) (V - \gamma v);$$

$$\therefore 1 = \left(1 + \frac{p}{P}\right) \left(1 - \frac{\gamma v}{V}\right).$$

Since  $p$  and  $v$  are assumed very small this relation may be written

$$1 = \left(1 + \frac{p}{P}\right) \left(1 - \frac{v}{V}\right)^\gamma;$$

$$\therefore PV^\gamma = (P + p)(V - v)^\gamma,$$

indicating that under adiabatic conditions,

$$PV^\gamma = \text{a constant.}$$

In the case of a perfect gas it has been shown that the isothermal curve is defined, for any temperature, by the relation,  $PV = RT$ .

In the same way, the adiabatic curve is defined by the relation,  $PV^\gamma = \text{a constant}$ , where  $\gamma$  is the ratio of the specific heats of the gas. For air,  $\gamma = 1.404$ , so that the equation of an adiabatic for air is  $PV^{1.404} = \text{a constant}$ .

The curve BF (Fig. 168) shows the adiabatic for which  $PV^{1.404} = 1$ . With it is shown, for comparison, the isothermal for which  $PV = 1$  (see Fig. 155).

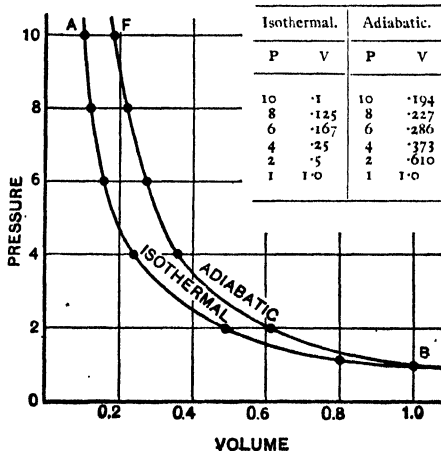


FIG. 168.

## 8. Relations Between Pressure, Volume, and Temperature in an Adiabatic Change

A relation has been established above which enables pressures and volumes to be calculated in an adiabatic change, viz.—

$$PV^\gamma = \text{a constant} \dots\dots\dots(1)$$

To obtain the temperatures, this relation must be employed in conjunction with the universally true relation,  $PV/T = \text{a constant}$ , where  $T$  is temperature on the absolute scale. Combining these two relations and eliminating  $V$ , a relation between pressure and temperature in an adiabatic change is obtained, viz.—

$$T.P^{\frac{1-\gamma}{\gamma}} = \text{a constant} \dots\dots\dots(2)$$



If, instead of eliminating  $V$ ,  $P$  is eliminated, a relation between volume and temperature in an adiabatic change is obtained, viz.—

$$TV^{\gamma-1} = \text{a constant} \dots\dots\dots (3)$$

**Example.**—AB (Fig. 155 and Fig. 168) is an isothermal for air at  $0^\circ \text{C}$ . What is the temperature of the isothermal through F, a point on the adiabatic, FB (Fig. 163), if the pressure at F is 10 atmospheres?

(1) Using the relation  $T \cdot P^{\frac{1-\gamma}{\gamma}} = \text{a constant}$ , this may be written—

$$\left(\frac{T_2}{T_1}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{\gamma-1},$$

where  $T_1$  and  $T_2$  are the initial and final temperatures,  $P_1$  and  $P_2$  the initial and final pressures. Thus—

$$\left(\frac{T_2}{273}\right)^{1.404} = \left(\frac{10}{1}\right)^{0.404}.$$

$$\text{Now } \log T_2 = \log 273 + \frac{0.404}{1.404} = 2.436 + 0.288 = 2.724;$$

$$\therefore T_2 = 530^\circ \text{A.}, \text{ or, the temperature} = 257^\circ \text{C}.$$

(2) Using the relation,  $T \cdot V^{\gamma-1} = \text{a constant}$ , this may be written—

$$T_1 \cdot V_1^{\gamma-1} = T_2 \cdot V_2^{\gamma-1},$$

and substituting the values of  $V_1$  and  $V_2$  from the table (Fig. 155),

$$273 \times 1^{0.404} = T_2 \times 0.194^{0.404}.$$

$$\text{Now } \log 273 = \log T_2 + 0.404 \log 0.194, = \log T_2 - 0.288;$$

$$\therefore T_2 = 530^\circ \text{A. as before.}$$

Thus it is seen that if a quantity of air, originally at  $0^\circ \text{C}$ . and atmospheric pressure, has its pressure increased suddenly to 10 atmospheres, the temperature rises to  $257^\circ \text{C}$ .

## 9. Experimental Determination of $\gamma$

(1) CLEMENT AND DESORMES.—Clement and Desormes devised a simple method for the determination of the ratio of the specific heats of a gas. The gas is enclosed in a vessel of badly conducting material at a pressure slightly higher or lower than the external atmospheric pressure. The vessel is fitted with a stopcock or tap, giving good communication with the outer air, so that on opening the stopcock the gas in the vessel undergoes a sudden change of volume, which under the conditions is approximately adiabatic. If the variations in the pressure and volume can be found, then from the relation,  $PV^{\gamma} = \text{a constant}$ , the value of  $\gamma$  can be obtained.

Let  $P_1$ ,  $V$ ,  $T$ , denote the pressure, volume, and absolute temperature of the gas in the vessel, and let  $P_1$  be greater than  $P$ , the

atmospheric pressure. On establishing communication for an instant between the interior of the vessel and the atmosphere, the internal pressure falls to  $P$  and a portion of the gas occupying a volume,  $V_1$ , of the vessel expands suddenly and, expelling the remainder of the gas, fills the vessel and so acquires a volume,  $V$ . The expansion is approximately adiabatic, and the temperature falls to  $T_1$ . The adiabatic curve,  $AB$  (Fig. 169), represents this expansion. Thus, the change has been made from the initial state given by  $P_1, V_1, T$ , to the state given by  $P, V, T_1$ , and of these quantities  $P_1, P, V$ , and  $T$  are known, but  $V_1$  and  $T_1$  cannot be measured directly. Connecting these two states is the adiabatic equation,

$$P_1 \cdot V_1^\gamma = P \cdot V^\gamma \quad \text{or} \quad \frac{P}{P_1} = \left(\frac{V_1}{V}\right)^\gamma.$$

If now the gas is allowed to remain in the vessel until its temperature rises to  $T$ , the initial temperature, the pressure will increase from  $P$  to  $P_2$ . The final state of the gas is given by  $P_2, V, T$ , and is indicated by the point  $C$  (Fig. 169), the change from  $B$  to  $C$  being approximately at constant volume, and  $C$  being on the same isothermal as  $A$ , for the final temperature is the same as the initial temperature. Then, since the gas is initially and finally at the same temperature,  $T$ , by Boyle's law—

$$P_1 V_1 = P_2 V, \quad \text{or} \quad \frac{P_1}{P_2} = \frac{V}{V_1}.$$

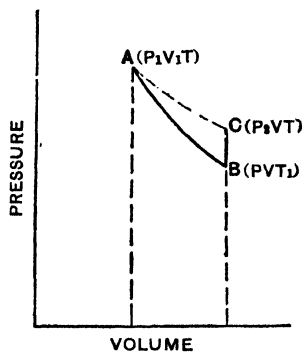
But, from the adiabatic equation,

$$\frac{P}{P_1} = \left(\frac{V_1}{V}\right)^\gamma;$$

$$\therefore \frac{P_1}{P} = \left(\frac{V}{V_1}\right)^\gamma = \left(\frac{P_1}{P_2}\right)^\gamma,$$

whence:—  $\log P_1 - \log P = \gamma (\log P_1 - \log P_2)$ ;

$$\therefore \gamma = \frac{\log P_1 - \log P}{\log P_1 - \log P_2}.$$



If  $P_1$ ,  $P_2$ , and  $P$  are very nearly equal, this relation becomes

$$\gamma = \frac{P_1 - P}{P_1 - P_2} \text{ approximately.}$$

A similar relation can be deduced if the initial pressure is less than the atmospheric pressure. The value of  $T$  does not enter into the final relations, but it may be obtained readily if required, for since the change from  $B$  to  $C$  occurs at constant volume,  $P_2/P = T/T_1$ .

*Experiment. Find the ratio of the specific heats of air by Clement and Desormes' method.*—Obtain a large bottle,  $A$  (Fig. 170), provided with a wide opening at the top and two side tubes. One of these tubes is fitted with a tap,  $T$ , the other is connected by thick rubber

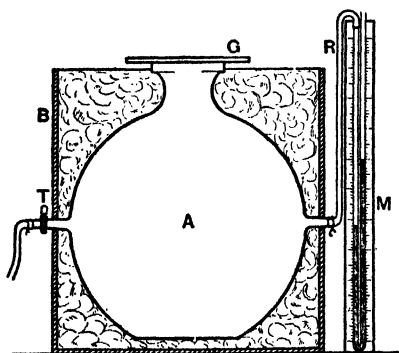


FIG. 170.

tubing,  $R$ , to a manometer,  $M$ . The opening at the top should have a good flanged surface, and this surface and a glass plate,  $G$ , which is used to close the opening, should be ground flat and smeared lightly with vaseline to make the connection gas-tight.  $A$  should be packed in a box with cotton-wool to protect it from draughts. The liquid in the manometer should have a very small density and a very small vapour pressure;

oil, glycerin, and sulphuric acid are suitable, the last having the advantage that it keeps the air in  $A$  dry. Mercury is not suitable, as owing to its great density the levels in the two limbs of the manometer would not differ much for small changes of pressure; and water is unsuitable because it charges the air in  $A$  with water vapour.

$G$  being well fitted to  $A$ , the air in  $A$  is compressed or exhausted by means of a pump attached to the side tube,  $T$ , until the manometer reading is considerable.  $T$  is then closed. The air is then allowed to remain for about five minutes in order to attain the constant temperature of the walls of  $A$ . When the reading of the manometer is stationary,  $G$  is removed for a second, air rushes out or in, as the case may be, and the pressure becomes atmospheric.

G is then quickly replaced. After about five minutes the air has again taken the temperature of the vessel and the final pressure may be observed.

It is important that the temperature of A should remain constant during the experiment, and that the gas should remain long enough in its initial and final states to take the temperature of the surroundings.

**Examples.**—(1) *With a Clement and Desormes' apparatus, using a water manometer, the initial and final pressures were greater than the atmospheric pressure by 40 mm. and 11 mm. respectively. The height of the barometer was 756 mm. Find  $\gamma$ .*

$P = 756 \times 13.6 = 1028$  mm. of water.  $P_1 = 1028 + 40 = 1068$  mm. of water.  $P_2 = 1028 + 11 = 1039$  mm. of water;

$$\therefore \gamma = \frac{\log 1068 - \log 1028}{\log 1068 - \log 1039} = \frac{3.0286 - 3.0119}{3.0286 - 3.0165}$$

$$\text{i.e. } \gamma = \frac{167}{121} = 1.38.$$

If the approximate relation is used, the atmospheric pressure need not be known, for if  $d_1$  is the difference of the heights of the manometer at the beginning of the experiment, and  $d_2$  the difference at the end,

$$d_1 = P_1 - P, \text{ and } d_2 = P_2 - P;$$

$$\therefore d_1 - d_2 = P_1 - P_2, \text{ i.e. } \gamma = \frac{d_1}{d_1 - d_2},$$

so that it is not necessary to determine  $P$ ,  $P_1$ ,  $P_2$  absolutely. Using this relation with the above data,

$$\gamma = \frac{40}{40 - 11} = \frac{40}{29} = 1.38.$$

(2) *With a Clement and Desormes' apparatus, using a water manometer,  $P = 1027$  mm. of water, and  $P_1$ ,  $P_2$  were less than  $P$  by 41 mm. and 12 mm. respectively. Find  $\gamma$ .*

Since the original pressure,  $P_1$ , was less than the atmospheric pressure,  $P$ , then at the adiabatic change air rushes into the vessel—that is, a volume of air equal to the volume,  $V$ , of the bottle at temperature,  $T$ , becomes a smaller volume,  $V_1$ . The temperature now is  $T_1$ , which is greater than  $T$ . After a while the temperature falls to  $T$ , and the pressure falls to  $P_2$ .

$$\text{For the adiabatic change, } P_1 V^\gamma = P V_1^\gamma.$$

$$\text{For the isothermal change, } P_1 V = P_2 V_1,$$

$$\text{whence } \gamma = \frac{\log P - \log P_1}{\log P - \log P_2},$$

a relation similar to the one obtained above. Using this relation with the data—

$$\gamma = \frac{\log 1027 - \log 986}{\log 1015 - \log 986} = \frac{3.0115 - 2.9949}{3.0064 - 2.9949};$$

$$\therefore \gamma = \frac{176}{125} = 1.41.$$

Using the approximate relation  $\gamma = (P - P_1)/(P - P_2)$  gives  $\gamma = 1.41$ .

There are several objections to Clement and Desormes' method. It is very difficult to close the mouth of the bottle at the exact instant when the internal pressure is equal to that of the atmosphere, and yet the time that elapses must be kept as short as possible or the change will not be adiabatic. Matters are complicated also by an oscillation of the air through the opening. Further, dry air must be used, as the presence of water vapour causes a low result.

(2) JAMIN AND RICHARD.—Jamin and Richard also determined the ratio of the two specific heats of a gas by a more direct method. A gas thermometer is constructed with the gas under investigation as the working substance. By passing an electric current through a spiral of platinum wire fused into the bulb, a known quantity of heat can be supplied to the gas either at constant volume or at constant pressure, and the increase of temperature deduced from the observed change of pressure or volume. If the *same* quantities of heat are supplied at constant pressure and at constant volume, and if  $t_p$  and  $t_v$  denote the corresponding increases of temperature, then

$$s_p t_p = s_v t_v \quad \text{or} \quad \frac{s_p}{s_v} = \frac{t_v}{t_p}.$$

The increases of temperature,  $t_p$  and  $t_v$ , are obtained by the usual gas thermometer method—that is,  $t_v = \frac{P}{P_0 \alpha}$ , where  $P$  is the observed *change* of pressure when the volume is kept constant,  $P_0$  the pressure of the gas at  $0^\circ \text{C.}$ , and  $\alpha$  the coefficient of increase of pressure with temperature at constant volume, and  $t_p = \frac{V}{V_0 \beta}$  where  $V$  is the observed *change* of volume when the pressure is kept constant,  $V_0$  the volume of the gas at  $0^\circ \text{C.}$ , and  $\beta$  the coefficient of expansion of the gas at constant pressure. Hence:—

$$\gamma = \frac{s_p}{s_v} = \frac{t_v}{t_p} = \frac{PV_0 \beta}{VP_0 \alpha} = \frac{PV_0}{VP_0}.$$

when, as for "permanent" gases such as air, etc.,  $\alpha = \beta$ .

#### 10. Calculation of the Value of $\gamma$ from the Velocity of Sound

The compressions and rarefactions which constitute a sound wave take place under adiabatic conditions, for the changes of density occur with great rapidity. Hence, in the relation which

gives the velocity of sound waves,  $V = \sqrt{\frac{E}{D}}$  (see Catchpool:

*Textbook of Sound*), in a medium of density,  $D$ ,  $E$  denotes the modulus of adiabatic elasticity.

In the case of a perfect or nearly perfect gas, such as air, it has been shown that  $E = \gamma P$ , where  $P$  is the pressure of the gas and  $\gamma$  the ratio of the two specific heats. Hence—

$$V = \sqrt{\frac{\gamma P}{D}},$$

and if  $V$ ,  $P$ , and  $D$  are known,  $\gamma$  may be calculated.

**Example.**—The velocity of sound in air at  $0^\circ \text{C.}$  is 33,200 cm. per sec. The density of air at  $0^\circ \text{C.}$  and 76 cm. pressure is 0.001293 gm. per c.c. Find  $\gamma$ .

In c.g.s. units,  $P = 76 \times 13.6 \times 981$  dynes per cm.<sup>2</sup>.

$$V = \sqrt{\frac{\gamma P}{D}}, \quad \gamma = \frac{V^2 D}{P};$$

$$\therefore \gamma = \frac{33200^2 \times 0.001293}{76 \times 13.6 \times 981} = 1.404.$$

## II. Work Done by a Gas During Expansion. Indicator Diagrams

When a gas expands at constant pressure, the work done by the gas is equal to the product of the pressure and the increase of volume (page 237). When a gas contracts at constant pressure, the work done on the gas is equal to the product of the pressure and the decrease of volume.

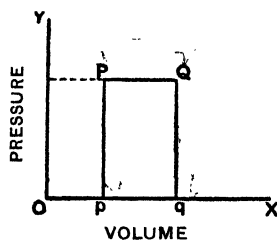


FIG. 171.

These facts may be represented graphically. Let  $P$  (Fig. 171) represent the initial state of the gas, volumes being represented by abscissae and pressures by ordinates, and  $Q$  the final state of the gas, the pressure being kept constant. Then the work done by the gas  $= Pp \times pq = \text{Area } PQqp$ . If  $Q$  were the initial state and  $P$  the final state, then the work done on the gas  $= \text{area } PQqp$ .

Suppose now the change from  $P$  to  $Q$  takes place at varying pressures, and let it be represented by the sloping line,  $PQ$  (Fig. 172). Then the whole area,  $PQqp$ , may be divided into small elements by lines parallel to the pressure axis. The work done in the change from  $P$  to a near point,  $R$ , is intermediate between the rectangular areas,  $Parp$  and  $bRrp$ , and, when  $pr$  is indefinitely small, approximates to the area,  $PRrp$ . Similarly for the other elements. The total work done during the expansion from the state,  $P$ , to the state,  $Q$ , is represented, therefore, by the area,

$PQqp$ —that is, the area enclosed by the ordinates,  $Pp$ ,  $Qq$ , the curve,  $PQ$ , and the volume axis. This is true whatever may be the nature of the path,  $PQ$ .

Suppose now that the gas is taken through a complete cycle of

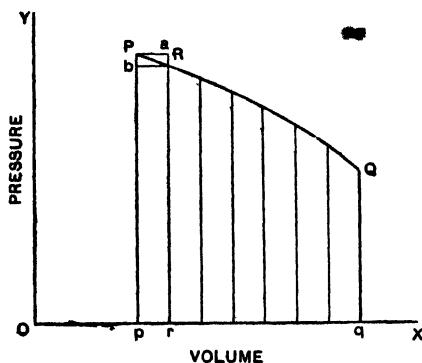


FIG. 172.

changes of pressure and volume such as is represented by the closed curve,  $PRQS$  (Fig. 173). If the cycle is traversed in a clockwise direction, the work done by the gas in the change from  $P$  to  $Q$  along the curve,  $PRQ$ , is given by the area,  $PRQqp$ , and the work done on the gas in the change from  $Q$  back to  $P$  along the curve,  $PSQ$ , is given by the area,  $QSPpq$ . Therefore in the

complete cycle the work done by the gas is given by the difference between the area,  $PRQqp$ , and the area,  $QSPpq$ —that is, by the area,  $PRQS$ . If the cycle is traversed in an anti-clockwise direction, the work done on the gas is given by the area,  $PRQS$ .

Such diagrams (Fig. 173) are called **indicator diagrams**, the most important example of which is that obtained from the steam engine. To obtain the diagram, a little cylinder opening out of the main cylinder contains a small piston which actuates a pencil to trace a curve on a drum. The drum rotates forwards and backwards perpendicularly to the

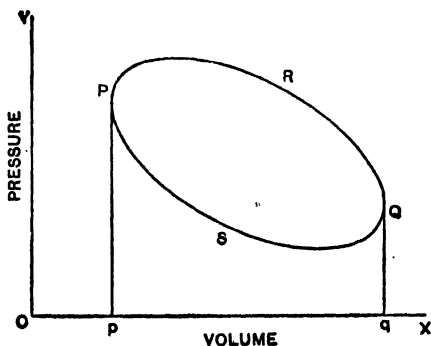


FIG. 173.

movement of the pencil as the main piston performs its outward and backward strokes. The small piston presses against a powerful spring so that its displacement is proportional to the

pressure of the steam in the main cylinder. In the form of curve usually obtained, S (Fig. 174) indicates the point when steam is first admitted to the cylinder; the main piston is still moving backwards. The pressure rises quickly to that represented by P. As steam is admitted gradually the main piston moves out with a constant pressure behind it, until the steam is cut off at the point indicated by R. Along RQ the piston is moving out with a gradually decreasing force behind it as the pressure of the steam decreases on expansion. At Q the exhaust is open and the piston moves back against the atmospheric pressure until it reaches the point represented by S, when steam is admitted again. The area, PRQS, is a measure of the amount of work done by the steam on the piston per stroke, and may be expressed in energy units if the scales of pressure and volume are known.

If the indicator diagram is plotted on graph paper, the areas may be estimated by counting squares or by one of the many other processes available. For a change such as that illustrated (Fig. 172), the work done by the gas is equal to the product of the average pressure and the increase of volume, and, when the increase of volume is very small, the average pressure is approximately the mean of the initial and final pressures.

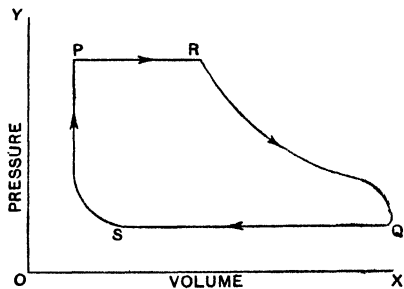


FIG. 174.

Again, if in a small change the volume remains approximately constant, the work done is equal to the product of the volume and the change of pressure. Also, it may be shown that the work done on a perfect gas during an isothermal change is given by:—

$$\text{Work} = P_1 V_1 \log \frac{V_1}{V_2} = P_2 V_2 \log \frac{V_1}{V_2},$$

and during an adiabatic change by:—

$$\text{Work} = \frac{1}{\gamma - 1} (P_2 V_2 - P_1 V_1),$$

in which  $P_1$ ,  $V_1$  apply to the initial state, and  $P_2$ ,  $V_2$  to the final state of the gas.



## 12. Heat Engines

The object of any heat engine is to supply energy to do useful work, and the working arrangement common to all types is to convert heat into mechanical energy, the heat being derived from various sources according to the type of engine. The heat is supplied to some *working substance* which is caused to do work by expanding. In practice, all engines are designed to give a maximum efficiency—that is, to supply the maximum amount of work possible from a given supply of heat. It is convenient, therefore, to consider the necessary working conditions for an *ideal* engine. Such an engine cannot be realised in practice, the nearest approach being the *Diesel* engine, which has an efficiency of about 0.32.

For the ideal engine the working substance is taken to be a perfect gas, and it will be seen that the working process must be *reversible*. A reversible process is one in which every part of the working system can be brought back exactly to its original condition by an exact reversal of the operations, and at every stage of the process a very small change in the external conditions will make it go the other way. For example, an adiabatic expansion can be exactly reversed, ideally; and also an isothermal change. The transference of heat by conduction, and the production of heat by friction, are, on the other hand, *irreversible* processes.

Again, the working process must embody a complete cycle of changes, so that the working substance at the end of the process is in exactly the same condition as at the commencement of the cycle. Such a cycle has been discussed above (page 274), the cycle being represented graphically (Fig. 173), and it was shown that for a closed cycle the mechanical work done by or on the gas during the changes is given by the area enclosed within the cycle. There are, of course, many possible cycles of changes, involving isothermals or adiabatics, or both, and such changes may be very complicated. It is obvious that the simpler the cycle, the simpler is the consideration of its effects.

## 13. Carnot's Cycle

In addition to a knowledge of the work done by or on the working substance in a cycle, the quantity of heat supplied or absorbed during the changes must be known. Heat energy is represented graphically most simply by adiabatics, since in passing through such a change no heat is extracted from or given up to the surroundings by the substance undergoing the change.

From the point of view of both work and heat, the most suitable form of cycle is made up of two isothermals and two adiabatics. It was shown by Carnot that this form of cycle would result in the greatest possible production of work. Carnot's essay on the subject of heat engines was of fundamental importance and forms the basis of all engineering practice.

A Carnot cycle may be represented in the form of an indicator diagram, ABCD (Fig. 175), by the intersections, AB, DC, of the two isothermals with the two adiabatics, AD, BC. Such a cycle is reversible, and can be traversed by the path, ABCDA, or by the path, ADCBA. The nature of the working substance is immaterial, provided that it changes in volume when heated, but it is simpler to consider it as a gas. The cycle cannot be followed actually in practice, but, again, theoretically, it can be followed very approximately by exaggerating somewhat the extent to which the parts of the mechanism employed possess certain properties, such as conductivity.

Starting with the working substance in the condition represented by D, it is first compressed adiabatically along DA; during this compression no heat enters or leaves the substance. From A to B the

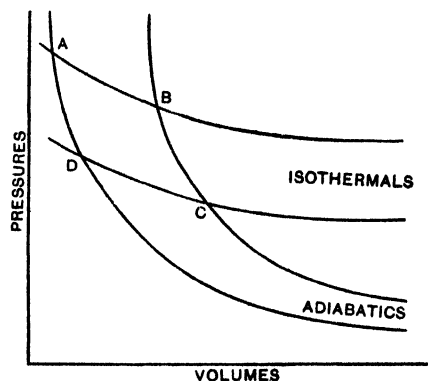


FIG. 175.

substance is made to expand isothermally; heat must be supplied to keep the temperature constant. From B to C the substance expands adiabatically; no heat enters or leaves, so that its temperature falls since it loses energy in doing work. Finally, from C to D the substance is compressed at constant temperature, heat being extracted from it in the process.

Throughout the cycle, work has been done on or by the substance. Heat changes occur, however, only along AB when heat is absorbed by the substance from its surroundings, and along CD when heat is abstracted from the substance by its surroundings.

Ideal mechanism is necessary for the performances of the stages in the cycle. The compressions and expansions must be carried out by means of a *frictionless* cylinder and piston. The adiabatic

compression from D to A must be carried out in a perfectly insulated enclosure; the walls of the cylinder and the piston must be made, therefore, of a material which is a perfect heat insulator; the base of the cylinder, however, is of a perfect conductor, and the cylinder is placed upon a stand which is a perfect insulator. The expansion stage from A to B requires that heat shall be absorbed by the substance to keep the temperature constant; for this purpose the cylinder must be transferred instantaneously to another stand, referred to as the *source*, which is maintained at a constant temperature and can supply any quantity of heat required. From B to C the expansion must be adiabatic again, so that the cylinder is again transferred instantaneously to the first insulating stand, and the temperature of the substance falls to that of the lower isothermal. Finally, from C to D, the compression being isothermal at the lower temperature, the cylinder must be transferred to a third stand, referred to as the *sink* or *condenser*, which is maintained at this constant lower temperature and can absorb any quantity of heat. The cycle of changes is thus completed.

The relation between heat and work in a Carnot cycle is obtained very easily.

The only heat changes that are involved are an absorption of heat by the substance from A to B, and an extraction of heat from the substance from C to D. If  $Q_2$  denote the amount of heat absorbed from the source, and  $Q_1$  the amount of heat given up to the sink, then the total heat received by the substance during the cycle is  $Q_2 - Q_1$ . Also, it has been shown that the total work done by the substance during the cycle is represented by the area, ABCD (Art. 12). At the conclusion of the cycle of changes the substance is in the same condition as at the beginning, and hence the total heat received, *expressed in work units*, must be equal to the total work done, *i.e.*

$$\text{Area ABCD} = J (Q_2 - Q_1).$$

In other words, by extracting an amount of heat,  $Q_2$ , from the source and giving up an amount of heat,  $Q_1$ , to the sink, the substance has been able to perform an amount of mechanical work represented by the area, ABCD. Since every operation in the cycle is reversible, the cycle could have been performed in the reverse order, DCBA. Then,  $Q_2 - Q_1$  would have been the total quantity of heat abstracted from the substance, in consequence of which an amount of work equal to the area, ABCD, would have been performed *on* the substance.

#### 14. The Efficiency of Heat Engines

In the cycle of changes considered above, a quantity of heat,  $Q_2$ , is absorbed from the source, and is thus available for conversion into work. Only a fraction of this quantity is utilised, however, since an amount,  $Q_1$ , is returned to the sink. Thus the fraction of  $Q_2$  which is ultimately converted into work is a measure of the *efficiency* of the engine. Thus:—

$$\text{Efficiency} = \frac{\text{Heat converted into work}}{\text{Heat taken from source}} = \frac{Q_2 - Q_1}{Q_2} = 1 - \frac{Q_1}{Q_2}.$$

The maximum efficiency is obviously unity, and the smaller  $Q_1/Q_2$  is made, the more nearly is the maximum value obtained. Also, it can be shown that if  $T_1$  and  $T_2$  are the temperatures of the sink and source, then  $Q_1/Q_2 = T_1/T_2$ , and thus:—

$$\text{Efficiency} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}.$$

Hence, the efficiency would be increased by making the temperature of the source very high and that of the sink very low. In practice, there is a limit to the lower temperature, the temperature of the atmosphere, and the efficiency can be increased only by making the temperature of the source as high as possible. The upper limit is determined by mechanical conditions and by difficulties of lubrication at high temperatures. The best possible cycle is that of Carnot, in which the heat is all taken in at the highest temperature, and rejection of heat takes place at the lowest temperature, the intermediate processes being adiabatic.

#### 15. The Second Law of Thermodynamics

No engine working between the same two temperatures can be more efficient than a reversible engine working on a Carnot cycle.

Suppose a reversible engine works between a sink at a temperature  $T_1^\circ$  and a source at  $T_2^\circ$ , and suppose it takes an amount of heat,  $Q$ , from the source per cycle and does work,  $W$ . If there is a more efficient engine working between the same temperatures, it means that if it absorbs heat,  $Q$ , from the source per cycle, it can do more work than  $W$ . Now suppose that this second engine is used to drive the reversible one backwards; the latter will act as a heat pump, giving heat,  $Q$  per cycle, to the source and requiring work,  $W$ , to be done on it. But it can do more work than  $W$  per cycle, so that it can drive the first engine and do other work as well.

It takes, however, heat,  $Q$  per cycle, only from the source, so that one engine returns as much heat as the other absorbs. Therefore, the two engines combined take no heat from the source, but can do an amount of extra work per cycle, and the process can continue indefinitely. By the First Law of Thermodynamics (page 240) the heat equivalent of this work must come from somewhere; it must have come, therefore, from the sink.

Again, it could be arranged that the more efficient engine performed work,  $W$ , just sufficient to drive the reversible engine. Then, it would absorb an amount of heat,  $Q'$ , from the source, less than  $Q$ . The combined engines would do no extra work, but an amount of heat,  $Q - Q'$ , per cycle would be transferred to the source, and this heat must come from the sink.

Thus it would be possible, by a continuous process, either to do work by absorbing heat from the sink, or to cause heat to pass from the cold body to the hot. Such a thing might be possible according to the First Law of Thermodynamics, but it is contrary to all experience that either of these things should happen. This statement is put forward in the hypothesis known as the **Second Law of Thermodynamics**, which may be expressed in one of two forms—

(1) According to **Clausius**:—*It is impossible for any self-acting mechanism, unaided by external agency, to transfer heat from one body to another at a higher temperature, or, heat cannot of itself pass from a colder to a warmer body.*

(2) According to **Kelvin**:—*It is impossible, by means of inanimate material agency, to derive mechanical work from a body by cooling it below the temperature of the coldest surrounding objects.*

The two forms of the law mean the same thing, and, if it is accepted, it follows that no engine can be more efficient than a reversible engine working between the same temperatures. Also, it follows that all reversible engines are equally efficient whatever the working substance; the only conditions which affect the efficiency are the temperatures at which it takes in and rejects heat. It should be noted that the law applies only to continuous operations.

The law is not capable of direct proof, but its truth is established because no experiment has ever been found to disprove it, and because predictions based on it have always been found to be correct.

## 16. The Absolute Thermodynamic Scale of Temperature

It has been shown above (Art. 14) that if any reversible engine takes in a quantity of heat,  $Q$ , at any particular temperature, the fraction of this heat converted into work during a complete cycle depends only on the temperature of the sink, and is greater the lower this temperature is made. The utmost effect which can be conceived, unless the First Law of Thermodynamics is rejected, is to convert the whole of this heat into work. Thus, if the temperature of the sink is reduced until the whole of the heat taken in is converted into work, *the lowest conceivable temperature*—an **absolute zero in every sense**—is attained. If the temperature of the sink is higher than this absolute zero, the fraction of the heat converted into work will depend solely on the temperatures of the source and sink and on nothing else.

Therefore, on the **absolute thermodynamic scale** temperatures are defined thus: If a reversible engine takes in a quantity of heat,  $Q_2$ , at one temperature,  $T_2$ , and rejects a quantity,  $Q_1$ , at the lower temperature,  $T_1$ ,

$$\frac{T_1}{T_2} = \frac{Q_1}{Q_2},$$

and, in the particular case just considered, when  $Q_1 = 0$ ,  $T_1 = 0$  also. The scale of temperature defined in this way is due to *Kelvin*. It is of great importance, since a scale is obtained which does not depend on the physical properties of any particular substance, and since a conception of the absolute zero of temperature which has a real physical meaning is obtained.

The above ratio alone is not sufficient to determine the values of  $T_1$  and  $T_2$ ; another relation is required to bring the thermodynamic scale of temperature into close connexion with another scale already defined in another way. Suppose it is agreed to arrange the new scale so that there is an interval of 100 degrees between the boiling point and the freezing point of water. Let  $T_2$  and  $T_1$  denote these temperatures. Then:—

$$T_2 = T_1 + 100.$$

It is known by experiment also that in this case

$$\frac{T_2}{T_1} = \frac{Q_2}{Q_1} = \frac{373}{273} = 1.366; \quad \therefore \frac{T_1 + 100}{T_1} = 1.366,$$

$$\text{i.e. } \frac{100}{T_1} = 0.366, \text{ and } T_1 = 273^\circ.$$

Thus the absolute thermodynamic scale of temperature is such that the boiling point of water is taken as  $373^{\circ}$ , and the freezing point of water  $273^{\circ}$ .

Further, considering the indicator diagram when a perfect gas is taken through a Carnot cycle, it can be shown that *the absolute thermodynamic scale of temperature coincides with the perfect gas scale*. The assumptions which must be adopted in this case are that in the case of a perfect gas (1) no internal work is done when the volume changes (page 237), (2) the gas obeys Boyle's law exactly at all temperatures (Art. 1). Then, by finding the work done during the cycle (Art. 11), it is found that the ratio of any two temperatures on the absolute thermodynamic scale is equal to the ratio of the two corresponding temperatures on the gas scale (page 108).

In practice, hydrogen or nitrogen is used in gas thermometers, and since the deviations of hydrogen and nitrogen scales of temperature from the perfect gas scale are very small, temperature measurements up to  $1600^{\circ}\text{C}$ . made with such thermometers are in good agreement with the absolute thermodynamic scale.

## 17. Entropy

The relationship which defines the absolute thermodynamic scale of temperature may be written in the form

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

If a substance at an absolute temperature,  $T$ , absorbs a quantity of heat,  $Q$ , it is said to receive an amount of **entropy**,  $\frac{Q}{T}$ . Using this definition, an engine working through a Carnot cycle (Art. 13) may be considered from another aspect. Suppose the system consists of a source at a temperature,  $T_2$ , and a sink at a temperature,  $T_1$ , the engine working between these temperatures. The source gives up an amount of heat,  $Q_2$ , to the working substance; it gives out, therefore, an amount of *entropy*,  $\frac{Q_2}{T_2}$ , and the working substance receives *entropy*,  $\frac{Q_2}{T_2}$ .

While the working substance is expanding adiabatically it neither absorbs nor rejects heat; thus, it neither gives nor receives *entropy*.

Next, the working substance rejects heat,  $Q_1$ , at  $T_1$ , and so it gives out *entropy*,  $\frac{Q_1}{T_1}$ ; at the same time the sink takes in heat,  $Q_1$ , at  $T_1$ , and so receives *entropy*,  $\frac{Q_1}{T_1}$ .

During adiabatic compression, again, there is no change of *entropy*.

But, in a Carnot cycle,  $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$ . Hence, the entropy lost by the source is equal to that gained by the sink, and the entropy taken in by the working substance is equal to that which it rejects. *For the system as a whole, therefore, there is no change of entropy; a certain amount has been transferred from the source to the sink, through the engine.*

This conception, which is of great use to the engineer in dealing with the behaviour of heat engines, is regarded as a definite physical property of a substance just as its temperature and its pressure are. It provides something which under certain conditions may be regarded as passing through a heat engine without altering in amount. In this sense it may be said to correspond to the electric current passing through an electric motor without altering in strength. The analogy, however, cannot be carried too far; entropy has the distinctive property that it tends to increase.

In engineering work it is usual to fix arbitrarily some particular state of the working substance as the starting point and call the entropy at that point zero. Values for the entropy of the substance at other states can then be found. Thus, in the case of steam, the starting point is taken as water at  $0^\circ\text{C}$ ., and tables have been drawn up by *Callendar* showing the entropy of unit mass of steam at various temperatures and pressures.

It will be seen that if a substance undergoes an adiabatic change, since no heat is supplied to or abstracted from the substance throughout the change, no change in the entropy of the substance takes place, *i.e.* along an adiabatic the entropy is constant (along an isothermal the temperature is constant). For this reason, adiabatic curves are sometimes called the *isentropic curves* for a substance (Art. 5).



## CHAPTER XIV

### LIQUEFACTION OF GASES

IT has been pointed out (page 196) that the properties of gases are continuous with those of unsaturated vapours at temperatures considerably above the boiling points of their liquids. Every gas, if its temperature is lowered sufficiently, will condense at some definite pressure to the liquid state. If, however, its temperature is not below its critical temperature (page 197), no amount of pressure will reduce it to a liquid. *The first requisite, then, in liquefying a gas is to cool it below its critical temperature; once below this temperature, the gas may be liquefied by the application of pressure only*, and the varying methods used by different investigators depend on the different means adopted to obtain the requisite amount of pressure and lowering of temperature.

#### 1. Early Experiments

The first well-authenticated successful attempts to liquefy gases were made by *Northmore* in 1806, who, using a brass condensing pump and glass receivers, succeeded in liquefying chlorine and sulphur dioxide. His work was passed over unnoticed, however, and it was not until 1823 that the next step was taken, when *Faraday* succeeded in liquefying several of the more easily condensible gases. In Faraday's earliest experiments, the materials from which the gas was to be generated were placed in one limb of the V-shaped tube (Fig. 176), and the other limb sealed off and placed in a freezing mixture. Heat was then applied to the limb containing the reagents, when the gas distilled over and condensed under the influence of its own pressure in the other limb.

About 1835, *Thilorier* succeeded in preparing large quantities of liquid and solid carbon dioxide by similar means. A large gunmetal retort, A (Fig. 177), swinging upon trunnions, contained sodium bicarbonate mixed with water, and a copper tube filled with sulphuric acid. An exactly similar vessel, B, was prepared to receive the liquid



FIG. 176.

carbon dioxide. The receiver having been surrounded by a bath of cold water, the gas was generated by tilting A and allowing the acid in the copper tube to mix with the sodium bicarbonate. The communicating tube, C, was then screwed into place and the stopcocks opened, when the carbon dioxide distilled over and condensed to the liquid state in B. By allowing the liquid carbon dioxide to escape

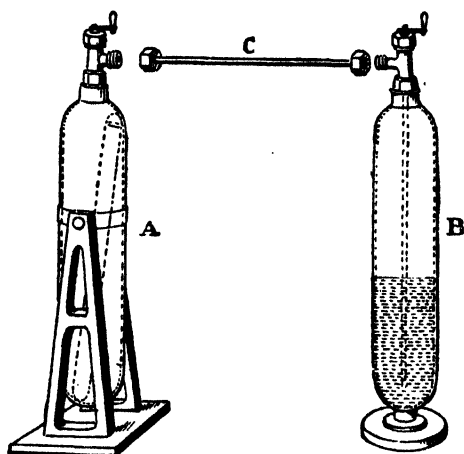


FIG. 177.

rapidly from a jet into a box of non-conducting material, Thilorier obtained solid carbon dioxide.

Using high pressures and the low temperatures which could be produced by a bath of solid carbon dioxide mixed with ether, Faraday succeeded in condensing several more gases to the liquid state, but oxygen, nitrogen, hydrogen, and one or two other gases resisted all attempts at liquefaction until 1877, when *Pictet* and *Cailletet*, working independently, announced the liquefaction of oxygen.

## 2. Pictet's and Cailletet's Methods

In Pictet's method, the oxygen was generated by heating potassium chlorate in the iron bottle, L (Fig. 178), which communicated with the closed tube, M. M was jacketed by a condenser, H, which contained liquid carbon dioxide boiling under reduced pressure. By this means a temperature of about  $-140^{\circ}\text{C}$ . was produced. As the carbon dioxide evaporated, it was drawn off by the pumps, E and F, and compressed into the cylinder, K, which was surrounded by liquid sulphur dioxide. The carbon dioxide was condensed to the liquid state again, and returned to the condenser, H, by the tube, k. Similar pumps, A and B, drew off the sulphur dioxide and condensed it in the receiver, D, which was surrounded by cold water. After the pumps had been working

continuously for some hours, a pressure of about 300 atmospheres being produced in M, the screw, N, was loosened suddenly, thus allowing the pressure to fall rapidly, and producing a still greater fall of temperature. It was then found that a small quantity of liquid oxygen had collected in M.

Cailletet's apparatus was constructed on a different principle. The gas under examination was confined over mercury in the thick-walled tube, T (Fig. 179), the open end of which was placed in a

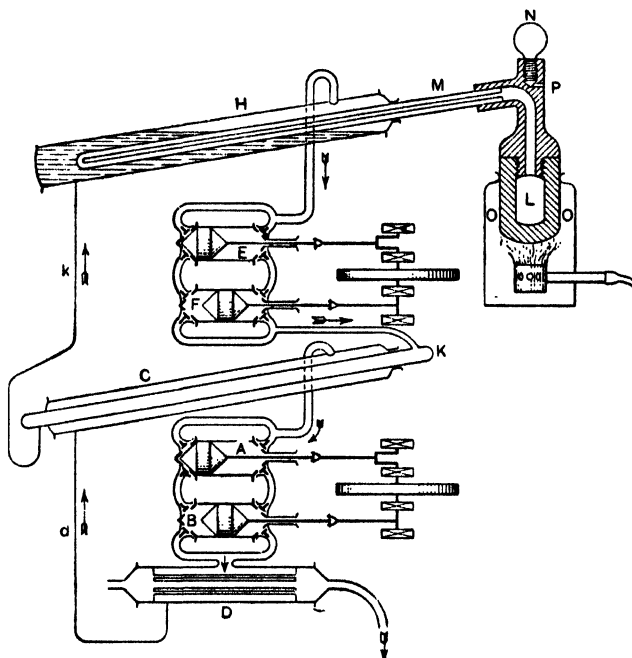


FIG. 178.

reservoir of mercury. The surface of the mercury was covered with water which communicated with the hydraulic pump, P. On working the pump, the mercury was forced into the tube, T, and the gas was strongly compressed. The pressure was then diminished suddenly by unscrewing the screw, V<sup>1</sup>, when the gas, now free to expand, forced the mercury back down the tube, T. Since the expansion took place with great rapidity, the change was almost adiabatic, and the heat equivalent of the work done in forcing back

the mercury was absorbed from the gas itself. This absorption of heat caused such a depression of temperature that a portion of the gas liquefied, and collected in drops on the sides of the tube.

### 3. Wroblewski and Olszewski's Method

By using liquid ethylene as a cooling agent, Wroblewski and Olszewski succeeded in obtaining liquid oxygen and liquid air in quantity. Liquid ethylene stored in the flask, *f* (Fig. 180), which was surrounded by a freezing mixture, passed through the spiral,

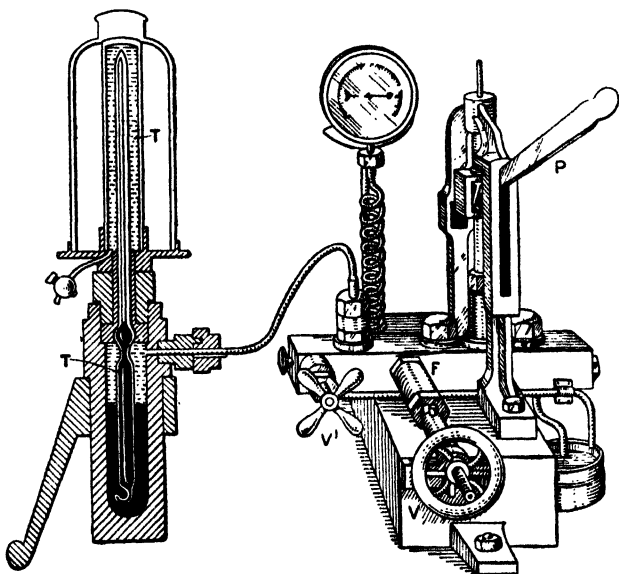


FIG. 179.

*g*, which was immersed in a bath of solid carbon dioxide and ether, giving a temperature of about  $-100^{\circ}\text{C}$ . By opening the stopcock, *h*, the cooled ethylene was allowed to flow into the vessel, *m*, where it surrounded the small flask, *a*, of about 200 c.c. capacity, which was destined to receive the liquid oxygen.

As soon as the liquid ethylene had covered completely the flask, *a*, the stopcock, *i*, which communicated with a large vacuum pump, was opened, and, by working the pump, the ethylene in *m* was caused to boil under greatly reduced pressure. In this way the

temperature of the ethylene was reduced continuously; when it had fallen below the critical temperature for oxygen, the stopcock, which communicated between the reservoir, *c*, wherein the gaseous oxygen was stored under pressure, and the small cylinder, *a*, was opened gradually. The oxygen passed over into *a*, and there, under the influence of the high pressure and low temperature, condensed to the liquid state and could be drawn off from time to time into the glass vessel, *e*. By using liquid oxygen as the cooling agent, in place of ethylene, the method was used successfully in liquefying hydrogen.

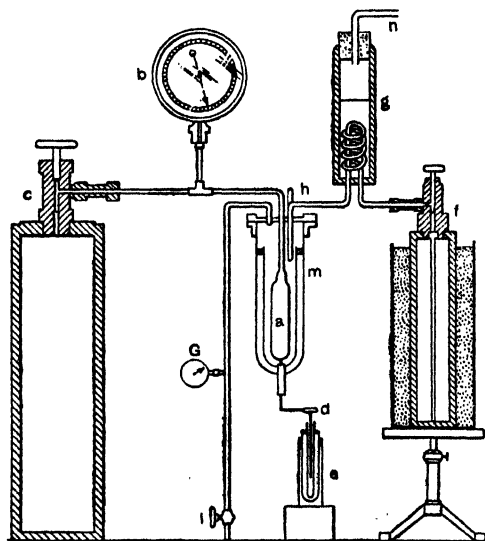


FIG. 180.

#### 4. The Joule-Thomson Effect—The Porous-Plug Experiment

The methods of liquefaction of gases described above are examples of the cascade process, in which the necessary low temperature is reached by successive stages, using an external refrigerating agent. The modern commercial process for the liquefaction of gases, however, is effected without the use of any external refrigerating agent, and the basis of

the process is the discovery, made by Joule, and by Joule and Thomson (Kelvin), of the cooling that may occur when a compressed gas is allowed to expand through a fine jet without doing external work.

The first experiments carried out by Joule have been described already (page 238), the apparatus being shown in Fig. 150. These experiments showed that very little or no internal work was done, Joule being unable to detect any fall of temperature. But the thermal capacity of the apparatus was so large in comparison with that of the gas that, unless the cooling effect was considerable, it

was likely to escape detection. The conclusion which might be drawn from the experiments was that there was no *large* cooling effect: but further investigation with more sensitive apparatus was necessary.

A more sensitive experiment, known as the *porous-plug experiment*, was carried out later by Joule and Kelvin, at the suggestion of the latter. In this experiment, the gas under observation was passed at a slow steady rate through a long copper spiral tube immersed in a bath at constant temperature. To the upper end, *aa* (Fig. 181), of this copper tube was attached a short tube of box-wood, *bb*, containing the *porous plug*. This plug consisted of cotton-wool, or silk fibres when high pressures were used, fixed by two perforated brass plates. A thermometer was placed in the exit tube, *ee*, with its bulb a short distance above the plug, this tube being of glass to permit the reading of the temperature. A metal vessel, *d*, filled with cotton-wool, surrounded the box-wood tube to protect the plug from the influence of external heat. It was found necessary to allow the gas to flow through the plug for about an hour before taking any readings, to make sure that a steady state had been reached.

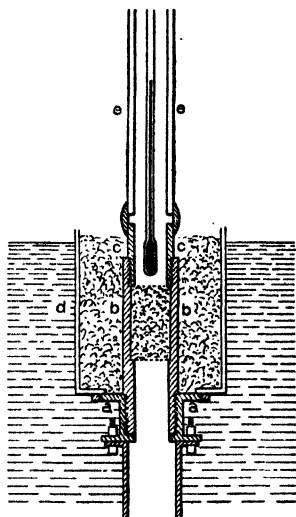


FIG. 181.

It was found that in the case of all gases, except hydrogen, there was a cooling effect, greater in the case of carbon dioxide than for air, oxygen, and nitrogen. In the case of hydrogen, however, there was a slight heating effect. In all cases, the effect was proportional to the difference of pressure on the two sides of the plug. The cooling effect with air was about  $0.25^{\circ}\text{C}$ . per atmosphere difference of pressure, and the heating effect with hydrogen about  $0.04^{\circ}\text{C}$ . per atmosphere. These results are consistent with the behaviour of the gases concerned with respect to Boyle's law, and may be explained by the deviations from Boyle's law (see page 257).

Suppose  $P_1$  is the pressure of the gas before passing through the plug, and  $P_0$  the pressure on the other side, which may be taken as

that of the atmosphere. Let  $V_1$  be the volume of the mass of gas passing through the plug in a certain time, under a pressure,  $P_1$ , and let  $V_0$  be its volume under the pressure,  $P_0$ . The passage of the gas from the high pressure to the low pressure side of the plug means an increase of volume,  $V_0$ , and work is done against the atmosphere, the amount of work done being given by  $P_0 V_0$  (page 237). But the volume of gas on the high pressure side has diminished, and work has been done on the gas in raising its pressure, and this work done is given by  $P_1 V_1$ . If the gas obeys Boyle's law,  $P_0 V_0 = P_1 V_1$ . This means that, as far as external work is concerned, there would be no reason for a change of temperature in the gas.

However, if there is some force of attraction between the molecules of the gas, some work would have to be done to separate the molecules in expanding from  $V_1$  to  $V_0$ . This additional energy would be obtained from the gas itself, and a fall in temperature would occur.

But no gas obeys Boyle's law absolutely, and, if  $P_1 V_1$  is not equal to  $P_0 V_0$ , there is an excess of external work to be accounted for.

Now, in the case of all gases except hydrogen, the value of  $PV$  diminishes with pressure, or the gases are more compressible than Boyle's law indicates. Hence,  $P_1 V_1$  is less than  $P_0 V_0$ , or the work done *on* the gas is *less* than the external work done *by* it. The energy required for the extra work done by the gas would be obtained from the gas itself, and there would be a cooling effect on this account. This cooling effect for any gas can be calculated from the values obtained by Amagat (page 260) and others for the variation of  $PV$ , and when this is done it is found to be very much less than that observed by Joule and Kelvin. It is evident, therefore, that there is a considerable cooling effect due to *internal* work.

For hydrogen,  $PV$  increases with pressure. Thus,  $P_1 V_1$  is greater than  $P_0 V_0$ , or the external work done *on* the gas is *greater* than that done *by* it. Hence, a heating effect due to this cause is obtained. This also can be calculated from the values obtained by Amagat for the deviations from Boyle's law, and it is found to be approximately the same as that observed by Joule and Kelvin. Thus, it is evident that in the case of hydrogen, the force of attraction between the molecules is very small.

## 5. Dewar's Method

The fact that a gas is strongly cooled by sudden expansion was utilised successfully by Dewar for the liquefaction of most of the

so-called *permanent* gases. The gas to be experimented on was stored under high pressure in steel cylinders. It entered the liquefier (Fig. 182) by the aperture shown on the right-hand side, passed up the tube, O, and round the spiral, S, which was cooled to a temperature of  $-70^{\circ}\text{C}$ . by immersion in a bath of solid carbon dioxide. The gas then passed down the inner spiral, D, into the tube, U, from which it escaped by a small jet. The escaping gas, cooled by the sudden expansion, swept back in the direction shown by the arrows over the exterior of the spiral, D, and cooled the down-coming gas to a still lower temperature; this portion of gas escaping at the jet flowed back and cooled a further part of the down-coming gas still more strongly. This cumulative process of cooling continued until the temperature of the gas was reduced below the *critical* temperature, when liquid began to drip from the jet, and was collected in the vacuum vessel, G.

#### 6. Linde's and Hampson's Method

The experiments of Dewar described above (Art. 5) were a most valuable advance in the development of the commercial processes for the liquefaction of gases. The credit of making use of the Joule-Kelvin effect, however, is attributed to Linde, of Germany, and Hampson, of England, who first introduced, independently, a process for obtaining liquid air and other liquid gases without the use of any external refrigerating agent, which was necessary in Dewar's method.

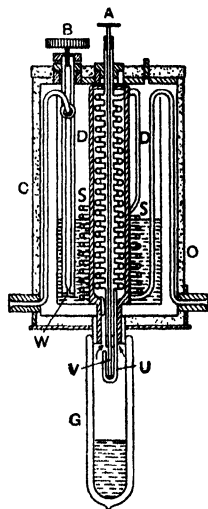


FIG. 182.

The apparatus employed by Hampson for the liquefaction of air is shown (Fig. 183). The air is drawn through the cylinder, A, which contains several trays of moist slaked lime, to remove carbon dioxide and water vapour, and passes into the pump, B. Here its pressure is raised to about 16 atmospheres, and it passes through the copper coil, C, to a second pump, D, where the pressure is further increased to about 160 atmospheres. The pumps, B and D, and the coils, C and E, are contained in tanks of cold water, which serve to absorb the heat generated by the compression of the gas. The compressed gas, after passing through the cylinders, F and H, in which all traces of water vapour are removed, enters the Hampson



liquefier. This consists of a series of concentric coils filling the whole space, KK, and terminating at the lower end in a jet, L, the opening of which is controlled by the screw and rod, M. The gas, passing down inside the coils, escapes at the opening, L, and is cooled; the cooled gas then flows back over the coils, cooling them still further, and emerges at P, from which it flows through R to the air inlet in A. In this way the temperature of the gas emerging from the jet gets lower and lower until the critical temperature is passed and liquid collects in the receiver, N.

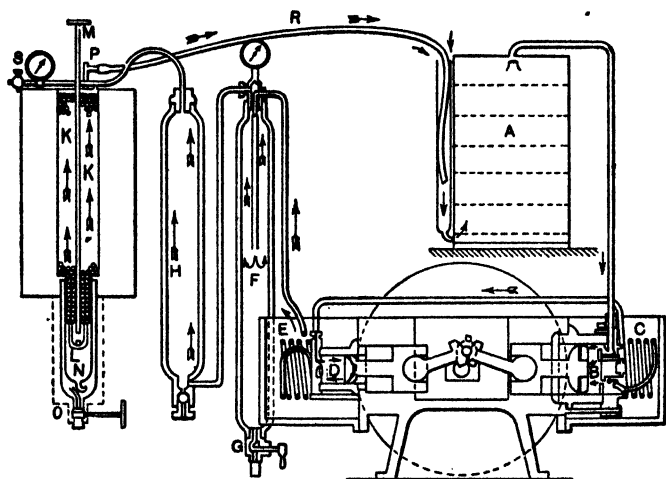


FIG. 183.

## 7. Liquefaction of Hydrogen

It was stated above (Art. 4) that, in the case of hydrogen, the Joule-Kelvin effect is positive; that is, a heating effect is shown on expansion. Joule and Kelvin found in their experiments that, in the case of gases showing a cooling effect, the effect diminished as the initial temperature of the gas was raised.

Later work has shown that for every gas there is a definite temperature at which the cooling effect becomes zero, and that above this temperature a heating effect is observed; that is, there is a temperature of *inversion* of the cooling effect. Olszewski found that for hydrogen this temperature was  $-80.5^{\circ}\text{C}.$ ; below this temperature there is a cooling effect, and above it a heating effect.

Thus, if the Joule-Kelvin effect is to be utilised in the liquefaction of hydrogen, the gas must first be cooled well below this inversion point by external means.

By using liquid air, boiling rapidly under reduced pressure, as a preliminary cooling agent, in place of the solid carbon dioxide (Art. 5), Dewar succeeded in liquefying hydrogen. In the modern process developed by Travers, the compressed hydrogen is cooled to about  $-200^{\circ}\text{C}$ . in successive stages, by passing through coils immersed in first a mixture of solid carbon dioxide and alcohol, then in liquid air, and finally in liquid air boiling under reduced pressure. After this it passed to a liquefier using the *regenerative* process as in the case of the liquefaction of air (Art. 6).

### 8. Liquefaction of Helium

For a long time this gas defied all attempts to liquefy it. Its critical temperature was not known accurately, and it was found to remain in the gaseous state even when compressed and cooled by rapidly boiling liquid hydrogen, about  $-260^{\circ}\text{C}$ ., and then allowed to expand suddenly. Also, like hydrogen, the Joule-Kelvin effect was found to be positive and the inversion temperature was not known accurately.

However, Kammerlingh Onnes spent several years in research work on the gas, and as the result of this work the gas was liquefied. The critical temperature was first determined, and found to be  $-268^{\circ}\text{C}$ ., from observations of isothermal curves at low temperatures, using Van de Waal's equation (see page 366). The inversion temperature for the Joule-Kelvin effect was found to be above the temperature of rapidly boiling liquid hydrogen, and it was concluded from this that it ought to be possible to apply the regenerative method successfully. Eventually, in 1908, an apparatus was designed and made by which gaseous helium, cooled to about  $-258^{\circ}\text{C}$ . by using rapidly boiling liquid hydrogen as a refrigerating agent, was allowed to expand from a pressure of about 200 atmospheres to one of about 40 atmospheres, and part of the helium liquefied, about 60 c.c. being obtained in the original preparation. The apparatus has been improved and used successfully in producing the liquid in sufficient quantities to enable its properties and physical constants to be determined, and to use it in experimental work.

The boiling point of liquid helium is  $-268.8^{\circ}\text{C}$ . under a pressure of 760 mm. of mercury. The liquid has been solidified, and its

freezing point at different pressures determined by **Keesom**, the lowest value obtained being  $-271.9^{\circ}\text{C}$ . at a pressure of about 20 atmospheres.

Liquid helium has been used principally in obtaining very low temperatures by evaporating it with very powerful pumps. In this way a temperature of  $-272.3^{\circ}\text{C}$ . was reached, or very nearly the *absolute zero*.

### 9. Uses of Liquefied Gases

When air is liquefied, both the oxygen and nitrogen pass into the liquid state simultaneously. When liquid air is allowed to evaporate slowly, however, nitrogen passes off in greater quantity than oxygen. The liquid which remains thus becomes richer in oxygen, and a ready means of obtaining comparatively pure oxygen is furnished.

By allowing liquid air to evaporate slowly and examining the spectrum of the last traces of gas given off, **Ramsay** and **Travers** discovered the rare gases *krypton* and *xenon*. Also the first traces of gas given off during the slow evaporation of liquid *argon* were found to contain *neon*.

The principal value of liquefied gases lies in their use as cooling agents, and the production of low temperatures. Thus, in establishing the gas scale of temperature as the practical standard, certain basic fixed points on the scale have been determined down to the boiling point of liquid oxygen at ordinary pressures ( $-182.97^{\circ}\text{C}$ .). Having determined an adequate series of fixed points with a gas thermometer, it is possible to measure low temperatures much more conveniently by means of resistance thermometers, and in the temperature range  $-190^{\circ}\text{C}$ . to  $0^{\circ}\text{C}$ . a standard platinum resistance thermometer is usually employed.

The variation of the electrical resistance with temperature of metals was investigated by **Dewar** and **Fleming** in the temperature range of liquid air and hydrogen, and the phenomenon of *superconductivity* was established. Copper and iron become almost perfect electrical conductors at  $-223^{\circ}\text{C}$ , and platinum at  $-240^{\circ}\text{C}$ .

## CHAPTER XV

### CONVECTION

**C**ONVECTION currents are set up in a fluid when the uniformity of density throughout its mass is disturbed by unequal heating. For example, when a mass of liquid is heated from below the portions first heated expand, and, becoming less dense than the surrounding liquid, are displaced upwards and give rise to an upward current from the point of heating. The liquid thus displaced upwards is replaced by the cooler liquid adjacent to it. In this way downward and lateral currents feeding the upward current are established. Similarly, if a gas flame or other heated body is placed in the middle of a room containing air at a uniform temperature, convection currents are set up at once. The air in the neighbourhood of the flame ascends and is replaced by air supplied by downward currents external to the ascending current.

Simple experiments may be performed to demonstrate these convection currents. (1) Place a few crystals of potassium permanganate at the middle of the bottom of a beaker of water and heat gently from below (Fig. 184). Note the ascent of the warm water up the middle of the beaker and the indraught of cold water from the top and sides: the stream lines along which convection occurs are indicated in colour. (2) In a similar beaker of water float a piece of ice and note the descending cold current from the melting ice and the indraught currents of warm water along the top towards the ice. (3) Light a Bunsen burner in a room in which the air is not disturbed by draughts: hold a piece of smoking paper near the burner, and note the upward direction of the convection current.

Change of density of a gas is accompanied by change of refractive index. This explains why, on a very hot day, distant objects lying

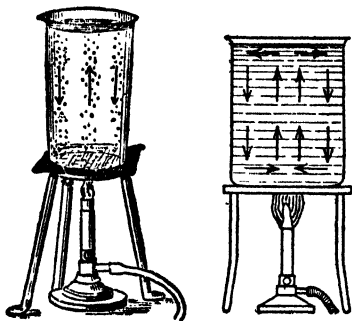


FIG. 184.

over the hot surface of the land viewed through the air appear to be quivering. The same appearance results when the objects in a room are viewed across the tops of burners or stoves. The twinkling of stars is explained in the same way.

### 1. Distribution of Heat by Convection

When a liquid in a vessel is heated from below, the convection currents set up establish a system of circulation in the liquid. Under this system the liquid circulates round and round, and every portion of it is brought in turn near the source of heat. In this way every part of the liquid is heated rapidly by the heat supplied at one point. It is for this reason that boilers are heated from below. In cold weather convection occurs in ponds and lakes because the surfaces are *cooled from above*.

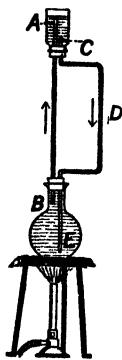


FIG. 185.

Again, when a body cools in air or other gas, the cooling is due partly to radiation, but mainly to convection. The circulation of the gas over the exposed surfaces carries heat away from the cooling body.

An application of convection currents is found in the system of heating buildings by hot-water pipes and by radiators: the principle is indicated by the following experiment:—

*Experiment.* Fit up a flask and a small bottle (Fig. 185) connected by tubing. Fill the flask with litmus solution and the bottle with dilute acid. Heat the flask gently. Note the ascending current of litmus in BA, and the descending current of acid in CDE as it issues at E. Note also that the circulating liquid quickly assumes a uniform red tint, showing the rapid mixing effect of the convective circulation. The experiment is more effective if the flask is filled with acid coloured with litmus and the bottle filled with alkali coloured with litmus, the quantities being adjusted to give exact neutralisation.

In practice the water in the boiler, which is placed at the lowest available position, is heated directly by the fire and rises through the outflow pipe, which emerges from the boiler at its highest point, and, circulating round the network of pipes, returns by the return pipe, which enters the boiler at its lowest point. The rapidity of the circulation depends on the difference between the average density of the water in the outflow pipe, from the boiler to the

highest point reached, and that of the water in the return pipes from the highest point to the boiler. This difference of density itself depends on the difference of temperature, which therefore should be as great as possible. For this reason the outflow pipe should pass vertically upwards as far as possible, so as to have a long vertical column of water at the highest possible temperature.

Heating buildings by steam is somewhat similar to the above. Steam is generated in a boiler, mains and radiators carry it round the building, and other mains bring the condensed steam back to the boiler. Heating buildings by hot air is another system now coming to the front. Air passes over hot plates in a chamber at the bottom of the building and convection currents arise which pass through gratings in the floor and walls of the room to be heated. Sometimes the air, drawn in by pumps, is sprayed with cold water and disinfected before passing on to the heating chamber, and thence to the building.

## 2. Ventilation

The simpler systems of ventilation are merely methods of establishing convection currents between the outside air and the air in the room to be ventilated, in such a way as to promote free circulation of the air without causing draughts. The principle applied in ventilation is illustrated experimentally:—

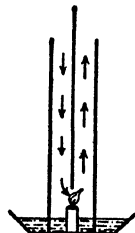


FIG. 186.

*Experiment.* Stand a lighted candle in a shallow dish, pour water round it, and place a tall glass cylinder, such as a lamp chimney, over it: the candle flame is extinguished. This is due to lack of ventilation; no air can pass underneath the chimney, and no air can flow down the chimney. Repeat the experiment, introducing down the chimney a T-shaped piece of metal or cardboard (Fig. 186): the candle continues to burn. There is a down-draught on one side of the T-piece and an up-draught on the other side. To show this, hold some smouldering brown paper near one side of the T-piece, and note the direction in which the smoke moves.

The draught in a chimney is a means of ventilation. The heated air ascends and is replaced by colder air from the room, and thus a fire in a room to which the outer air has access is an effective means of ventilation. As it is of great importance that the true cause of convection in liquids and gases should be understood, this particular case of the draught in a chimney when a fire is lighted at the bottom may be considered in detail:—

Suppose a chimney stack (Fig. 187) stands, say, outdoors. When a fire is lighted on the hearth, the air immediately above the fire is heated and therefore expands. This expansion forces some of the air in the front of the fire outwards. At this stage, suppose an imaginary diaphragm, XY, is stretched across the mouth of the fireplace; and consider the pressures on the two sides of XY. Take two points, A, B, on the same level near the top of the chimney, A being over the mouth of the chimney and B just outside the chimney, and two points, D, E, on the same level on either side of XY. Draw AC, BF perpendicular from A, B, cutting the horizontal through D, E, in C and F. Let H be the point where AC enters the region of hot gas near the fire. Then, if P is the pressure of the air at A, B,  $d$  the density of the air lying along AH and BF, and  $d_1$  the density of the hot gas in the region, HCD,

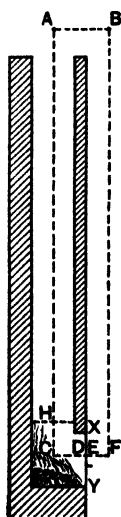


FIG. 187.

$$\text{Pressure at D} = P + AH \cdot dg + HC \cdot d_1 g,$$

$$\text{Pressure at E} = P + BF \cdot dg;$$

$$\therefore \text{Difference of pressure at D and E} = HC (d - d_1) g.$$

The density,  $d$ , is greater than  $d_1$ , and  $(d - d_1)$  is positive. Thus, there is a force acting from right to left across XY, and as a result of this force the diaphragm, XY, is forced towards the fire. Or, if the diaphragm is removed, air from outside is forced into the neighbourhood of the fire. The region, HC, of hot gas thus extends gradually, the pressure difference at XY gradually increases and is a maximum when the whole chimney is full of hot gas. Thus the draught up the chimney gradually increases until the fire is at its height.

When a number of people are in a room, the air in their immediate neighbourhood is rendered less dense than the remainder of the air (1) by the rise of temperature, (2) by the presence of water vapour from the breath (page 216). This air rises, as explained above, to the upper part of the room. If there is no exit for this hot impure air it gradually accumulates, and the room becomes *stuffy*. Ventilators (openings) should be provided, therefore, at the top of the room for the exit of this gas, and ventilators near the floor of the room for the inlet of fresh air.

If there is an open fire in the room, the chimney serves as an exit for most of the gas. If, however, the incoming fresh air is

not mixed thoroughly with the air of the room, there is likely to be a cutting draught in the room and the upper part of the room will remain foul. The *Tobin tube*, T (Fig. 188 (a)), was one of the early devices designed to remedy this state of affairs. The tube communicates with the outer air at its lower end, and at its upper end with the room about five feet from the ground. The draught up the chimney, C, causes air to rise up the Tobin tube, and this air thoroughly cleanses the upper part of the room before also taking its departure up the chimney. In some cases the Tobin tube is built around the chimney so that the incoming air is warmed, without being fouled, before it enters the room.

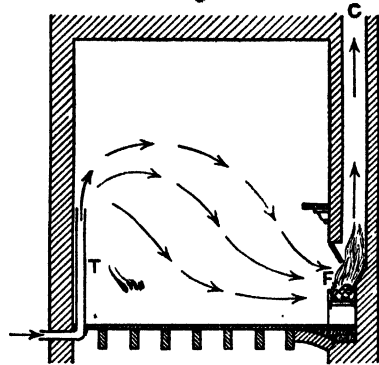


FIG. 188 (a).

Another early device suitable for rooms having no other rooms above them was the *McKinnell's ventilator* (Fig. 188 (b)). It acts as an inlet and outlet: the inner tube forms an outlet and the space between the tubes forms an inlet.

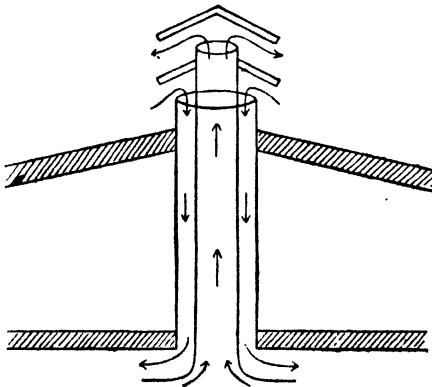


FIG. 188 (b).

In these days of the cult of the open window the Tobin tube and other early, and more or less similar, simple devices are losing favour, although they are still sometimes employed: moreover they are inadequate for cinemas, theatres, and other places where large numbers of people congregate. In these cases in particular, mechanical methods of ventilation in which

fans and pumps are used to circulate the air are employed. Thermal convection, however, plays little part in these, and they are therefore beyond the scope of this book.



### 3. Winds

Wind is air in motion, the motion being due either to convection, or to the rotation of the earth, or both. The more familiar phenomena of winds are good examples of convection currents set up in the atmosphere by unequal heating.

**LAND AND SEA BREEZES.**—Land absorbs solar heat more rapidly than water, and, owing to its smaller specific heat (page 124), is raised to a higher temperature by the heat thus absorbed. For the same reason, land loses heat more rapidly than water. Hence, during the day land is heated by solar radiation to a greater degree than the sea, and the air in contact with it also is heated,

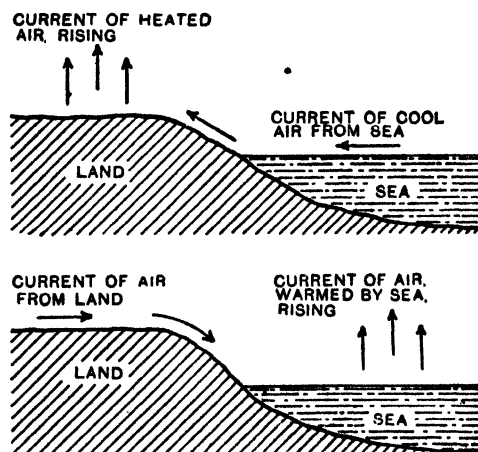


FIG. 189 (a).

expands, and, rising, is replaced by cooler air from over the sea, thus causing a *sea breeze*. After sunset, however, land cools more rapidly than the sea, and ultimately the air over the land becomes colder than that over the sea; the direction of the current of air is reversed, and during the night a *land breeze* prevails (Fig. 189 (a)).

#### THE TRADE WINDS.

—The surface of the earth within the tropics is heated greatly by the sun, and the heat is communicated to the air in contact with the earth, causing it to ascend. To replace this air, a current of colder air sets in from the polar and temperate regions, thus tending to produce a north wind in the northern hemisphere, and a south wind in the southern hemisphere. To determine the actual direction of the wind, however, it is necessary to consider also the rotation of the earth from west to east. By using the known velocity of the earth at any point on its surface and applying the Parallelogram of Velocities, the magnitude and direction of the velocity of the wind relative to the surface of the earth may be found. By this means it is found that a north-east

wind is produced in the northern hemisphere and a south-east wind in the southern hemisphere. These winds are known as the **trade winds**. The directions of the trade winds vary, of course, with the latitude and the shape of the surrounding coasts.

In *Meteorology*, the two factors usually measured in connexion with wind are (1) the direction from which it is blowing, and (2) its velocity or *force*. The direction is given by wind-vanes, smoke, etc., and the velocity is estimated by noting its physical effect on surrounding objects such as trees, etc., or measured by using an *anemometer*. The usual form of the apparatus is **Robinson's cup anemometer**. It consists of four hemispherical cups attached to the ends of two crossed metal arms (Fig. 189 (b)). The cross is pivoted at its central point in such a way as to be free to rotate in a horizontal plane. The difference of pressure of the wind on the convex and concave surfaces of the cups causes the cross to spin round. The number of revolutions of the cups in a given time is proportional to the amount of wind which passes them, and the total number of revolutions is recorded on a dial graduated to read to "miles of wind." The more elaborate forms are arranged to give a continuous record, in the form of a graph.

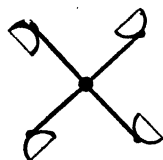


FIG. 189 (b).

#### 4. Ocean Currents

If any part of the ocean is subject to winds of constant, or nearly constant, force, the result must be to blow the surface waters in the direction in which the wind blows and thus give rise to drift currents. For example, the trade winds by their constancy have such an effect on the waters of the equatorial belt. Both the N.E. and S.E. trade winds tend to drive the surface waters at the equator towards the west, and thus give rise to the *Atlantic and Pacific Equatorial Drift Currents*. If there were no obstructing lands, these currents would flow continuously round the earth. As it is, however, when they reach the western boundaries of their oceans, they are deflected in directions determined by the configuration of the land.

Consider the Atlantic Equatorial drift. It is a wide belt of hot water about 50 fathoms deep, blown across from the African side at the rate of some 18 miles per day. On reaching the wedge-shaped coast of Brazil it is divided, one small branch proceeding southward, but the greater part travelling along the northern coast, and between it and the West Indian islands, into the Gulf of Mexico. Here it is greatly converged and accelerated as by a funnel, and,

sweeping round the gulf, it issues from the narrow Florida Strait with a speed of about 4 miles per hour, about five times its original speed, and still retaining so much heat that its temperature ranges from  $77^{\circ}$  to  $83^{\circ}$  F. It is known as the *Gulf Stream* (Fig. 190), and flows in a north-easterly direction across the Atlantic. Even off the Newfoundland Bank, when it has travelled more than 2000 miles from its point of origin in Florida Strait, its temperature is  $20^{\circ}$  to  $30^{\circ}$  F. above that of the surrounding water, on which it accordingly floats. Its speed, however, is reduced greatly by its spreading out in a fan shape.

So far it may be considered to have travelled under the original impulse derived from the trade winds, but when this force has nearly ceased to be effective it reaches the region of prevalent S.W.

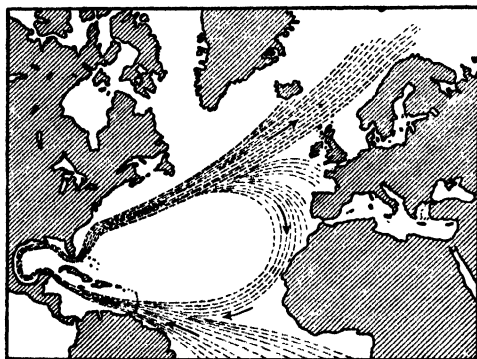


FIG. 190.

winds, by which it is carried on in the same N.E. direction until it reaches the western coasts of the British Isles, France, and Norway, where its influence in mitigating the severity of the winter in those countries is very great. The ports of western Norway are never ice-bound, whereas those much further south on the Baltic coast of

Sweden, to which the warm waters of the Gulf Stream do not penetrate, are frozen up regularly for months every winter. It is the very high specific heat of water that enables the Gulf Stream to give out so much heat to the countries washed by it.

A large number of ocean currents are surface drifts due to the action of prevailing winds, like the Gulf Stream when it reaches N.W. Europe, but some are due to convection. Thus, the cold in the Arctic regions causes water to sink and flow towards the equator as a deep current, while the surface water at the equator flows towards the poles, to replace the water carried away by this under-current.

Much work has been done in recent years to elucidate the effect of the Gulf Stream on the climate and fisheries in N.W. Europe.

## 5. The Atmosphere

The earth's atmosphere is subject to incessant mixing by winds and also to solar radiation, with the result that it is very far from being in a state of thermal equilibrium.

If a quantity of air is carried upwards by atmospheric disturbances, its pressure is diminished, and the relations between pressure, volume, and temperature in an adiabatic change (page 267) show that its temperature falls also, even if no heat transference takes place with other air.

**Example.**—If the air rises 100 m., its pressure falls by about  $1/80$  of an atmosphere. Hence, its absolute temperature is multiplied by about

$$\left(1 - \frac{1}{80}\right)^{\frac{\gamma-1}{\gamma}} = 1 - \frac{\gamma-1}{\gamma} \frac{1}{80} = 1 - \frac{0.285}{80}, \text{ since } \gamma = 1.4.$$

That is, the fall of temperature per 100 m. ascent is approximately

$$\frac{0.285 \times 273}{80} = 1^\circ \text{C.}$$

The effect of conduction is comparatively negligible. Convection does not equalise temperatures because the warmer lower strata are at a greater pressure, and therefore denser, than the colder layers above; and if they were made to rise, they would become as cold.

The temperature of the atmosphere at different levels has been studied by means of balloons provided with apparatus for registering the temperature and elevation. The results of such investigations have led to the conclusion that the atmosphere which is a thin layer, relative to the size of the earth, consists of two parts—the lower, known as the *troposphere*, and the upper, the *stratosphere*—and that there is no gradual change from one layer to the other, the surface of separation, known as the *tropopause*, being sharply defined.

In the troposphere the temperature falls with the elevation, and for any given altitude the temperature is higher over the equator than over the poles. Also the height of the layer varies from about 20 kilometres over the equator to about 6 kilometres at the poles.

In the stratosphere there is very little change of temperature with height, and for any given altitude the temperature is higher over the poles than over the equator.

## 6. Cyclones and Anticyclones

A cyclone is a region of low barometric pressure, an anticyclone a region of high barometric pressure. Observations of the barometric pressure, together with observations of wind changes, enable

the meteorologist to make predictions of weather for a day or two ahead.

Warm currents are found to originate in the equatorial regions and cold currents in the polar regions. During their passage these currents undergo gradual modification. Thus, the north polar air, very clear, free from dust and moisture, begins cold and stable, but the lower layers become warm over the Atlantic and ascending currents result. The damp equatorial air, on the other hand, comes from the dusty tropical regions with increasing humidity. When these two air currents meet, a **cyclonic system** is formed by the tendency to produce stability, the warm air being lifted and the cold air subsiding below it, increased pressure being produced on the windward side and decreased pressure on the leeward side,

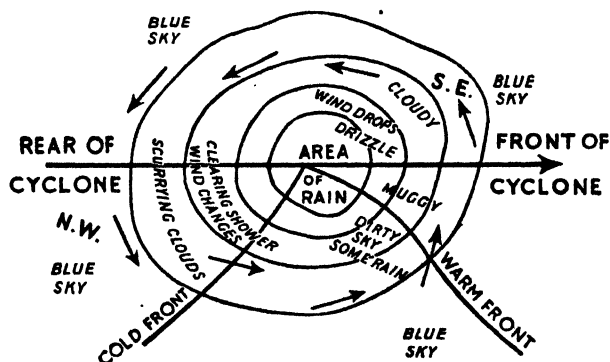


FIG. 191 (a).

and the air circulates round the low pressure region. These cyclonic systems are not stationary but take up the general motion of the atmosphere as a whole. Thus, since the prevailing winds in these latitudes are westerly, cyclones are moving constantly to the east.

Such cyclonic systems are studied by plotting on a map of an area, say Europe, pressure readings observed at a number of stations throughout the area, and drawing **isobars**, or *lines of equal pressure*, for every change of pressure of 0.2 inch. These lines are found to be closed curves, fairly regular, and nearly concentric with the area of lowest pressure, and the wind appears generally to follow the isobars. As a cyclonic system passes over a region, a variety of weather changes is experienced. These changes follow a definite order, and the system takes anything from one to five days

to pass over, the rate of motion being calculated from the observations made by the various stations.

The general form of a cyclonic system is illustrated (Fig. 191 (a)), and the general nature of the weather changes involved is indicated. Note particularly that in a cyclone the pressure is lowest in the centre.

An anticyclonic system can be dealt with in a similar manner, and used to predict weather conditions, though the formation of such a high-pressure system is not explained easily. There will be a region of high pressure between two cyclonic systems which may give rise to anticyclonic conditions. Another suggested explanation

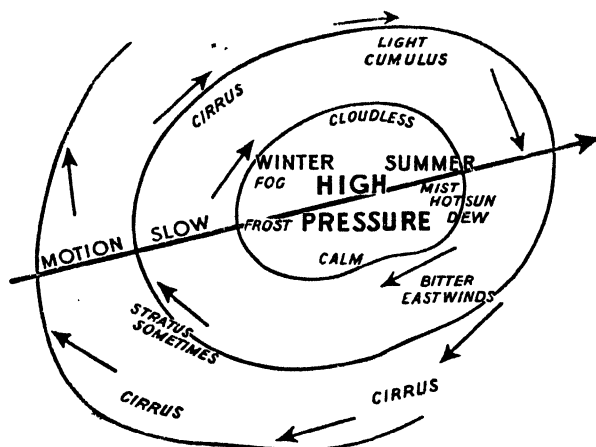


FIG. 191 (b).

is that an anticyclonic system is due to a mass of still air being brought bodily from tropical regions. Such systems are very stable, move very slowly, and will exist over an area for a long period.

The typical form of an anticyclonic system is illustrated (Fig. 191 (b)), together with the usual weather conditions associated with it. The chief characteristic is a cloudless sky, and the pressure changes are usually very small so that the wind is very light. Note particularly that in an anticyclone the centre is the region of high pressure.

Note again the directions of the winds in the various parts of a cyclone and anticyclone. They are found to obey a law known as

**Buys Ballot's Law**, which states that in the northern hemisphere the winds in a cyclone blow in an anticlockwise direction around the centre of low pressure (they blow, in fact, in anticlockwise *spiral* curves around and at the same time towards the low pressure centre), whilst in an anticyclone they blow in the opposite direction to those in a cyclone, that is clockwise round the centre of high pressure. Another useful rule for remembering the direction of the wind in the above cases is as follows:—"Stand with the low pressure on your left hand: then the wind will blow against your back." These statements apply to the northern hemisphere: for the southern hemisphere the rules are opposite, *e.g.* substitute "face" for "back."

## CHAPTER XVI

### THERMAL CONDUCTION

HEAT may be transferred from one point to another in three different ways—*conduction*, *convection*, *radiation*. In *conduction*, heat imparted to any part of a body sets the molecules of that part of the body in more energetic vibration. These transmit the vibration to the neighbouring molecules, and thus the heat travels slowly through the body. In *convection* (Chapter XV.), which is possible only in fluids—liquids and gases—the parts heated expand, and, becoming less dense, rise and carry the heat *by their own motion* to other parts. In *radiation* (Chapter XVII.), the hot body imparts its vibration to the ether; waves are set up which travel outwards in all directions with an enormous velocity, and through vacuous spaces even more freely than through air or other matter.

#### I. Substances Differ in Thermal Conductivity

The fact that heat may be transmitted or conducted through the substance of a body is familiar from everyday experience. When the end of a poker is placed in a fire, the heating effect is not confined to the portion actually in the fire. The portion outside the fire is heated also in a way which indicates that heat must be conducted through the substance of the poker from the end in the fire towards the other end. Again, when boiling water is poured into a metal vessel, the *outside* of the vessel becomes hot quickly, showing that heat has been conducted through the thickness of the metal walls. Also, when a fire is lighted in a closed range, the portions of the range not in direct contact with the fire become heated by the heat conducted from the fire through the metal of the stove. Lastly, if a flat-iron or block of any substance is placed on the hot-plate of a stove, it becomes heated throughout its mass by the conduction of heat from its under surface.

The power which a substance possesses of allowing heat to be conducted through it is known as the **thermal conductivity** of the substance.

Substances differ greatly in their power of conducting heat. A rod of wood, if placed with one end in a fire, gives little indication



of the conduction of heat outwards from the end in the fire. Also, if boiling water is poured into a thick wooden vessel, the heating of the outer surface takes place very slowly and is very slight. The difference of the heat sensations experienced on touching different substances (Chapter I., Art. 1) is also due to difference in the conductivity of the substances: as already explained, the good conducting substances such as metals conduct heat rapidly *to* or *from* the hand and thus cause a more marked sensation of heat or cold. The following experiments illustrate further the difference in the conductivity of different substances:—

*Experiments.* (a) Fit the end of a short wooden cylinder into a thick brass tube of the same external diameter. Wrap a piece of *thin* paper round the cylinder at the junction of the wood and brass, and hold the paper in the flame of a Bunsen burner. It will be found that the paper over the wood is scorched badly, while that over the brass is not scorched. This is due to the fact that the brass, being a good conductor, conducts the heat away from the paper sufficiently rapidly to prevent scorching, whereas the wood, being a poor conductor, is unable to do this. If the paper be *thick* it will be found that it is scorched wherever the flame touches it. The low conductivity of the paper prevents the heat from being transmitted *through its thickness*, and the presence of the good conducting brass beneath therefore has no effect on the result.

(b) Take similar strips of silver, copper, and iron, and place them with one end in hot water in a beaker. The other end of the silver strip soon becomes very hot; the copper also gets hot, but not to the same degree as the silver, while the iron strip is heated to a much less extent than either the silver or the copper.

The fact that some substances have a low conducting power has many familiar applications. Handles of wood or other badly conducting material are provided usually for tools, hot-water vessels, and other appliances where the hand must be protected from heat which otherwise might reach it by conduction. In the case of kettles, tea-pots, coffee-pots, etc., the handle is sometimes of metal, but is separated from the body of the vessel by discs of china or other badly conducting substance. The efficiency of clothes and bed clothing is due to the low conductivity of the air in the material, and of the material itself: the heat developed in the body is prevented from escaping by the covering of badly conducting material, and thus the feeling of warmth is maintained.

A good example of the retention of heat by a hot body surrounded by a bad conductor is found in a *Norwegian cooking box*, which consists of a wooden box with a thick lining of felt, so arranged as to leave a central cylindrical space into which a vessel containing food fits. The food is cooked partly over the fire in this vessel, and while still hot is placed in the box. The lid, also felt-lined, is closed tightly over it. The heat is maintained so well that the cooking is completed in the box, and after an interval of some hours the temperature will have fallen only a few degrees.

Bad conductors are as effective in keeping a body cool as in keeping it warm. Thus a covering of felt or flannel which will keep a vessel of hot water from cooling will also keep a piece of ice from melting. In the one case heat is prevented from passing out from the water, and in the other from passing into the ice.

A vacuum is a perfect non-conductor of heat. Double-walled vacuum vessels of glass are now made (Fig. 192), consisting of a flask or tube inside another. The two are sealed together at the top, and the space between them exhausted of air as completely as possible through a fine tube at the bottom of the outer vessel, which is then sealed off. As a rule the surfaces of the vessels next the vacuum are silvered to prevent loss or gain of heat by radiation (page 348). These vessels were designed for the storage of liquefied gases which would boil away at once if placed in ordinary vessels. Liquid air may be kept for days in a good vacuum vessel. They are used largely also in the form of "Thermos" flasks for keeping hot drinks hot and cold drinks cold for a long time.

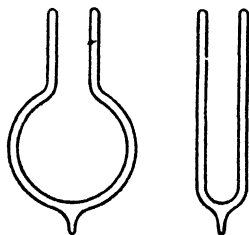


FIG. 192.

## 2. The Davy "Safety" Lamp

When a flame is applied to gas issuing from a jet, the temperature of the gas is raised above its temperature of ignition, and combustion commences, continuing so long as a supply of oxygen is obtainable and the temperature remains above the ignition temperature of the gas. If, however, a piece of good conducting material is placed in a flame, it may conduct heat away so rapidly that the temperature falls below the temperature of ignition and combustion ceases. This effect is illustrated by the following experiments:—

**Experiments.** (a) Take a piece of thick copper wire and coil it into a spiral of about 5 mm. internal diameter. Light a candle, and when the flame is burning strongly lower the spiral of copper wire on to the wick of the candle. The flame is extinguished at once.

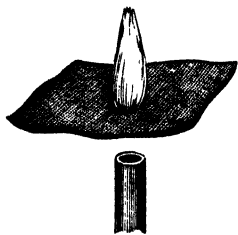


FIG. 193.

(b) Take a piece of clean copper gauze of medium mesh, and lower it on to the flame of a Bunsen burner. It will be found that the flame does not get through the gauze. As the gauze is lowered, the flame is kept below it, and may be extinguished completely by lowering the gauze on to the burner. The gauze conducts the heat away from the portion of the flame in contact with it sufficiently rapidly to lower the temperature below that at which combustion takes place, and the region of combustion, therefore, cannot extend above the gauze.

(c) Hold a sheet of copper gauze about an inch above a Bunsen burner, and light the flame *above* the gauze (Fig. 193). It will be found that the flame appears only above the gauze, and is prevented by the thermal conductivity of the copper from extending below it.

The principle illustrated by these experiments was utilised in the construction of the **Davy** safety lamp, of which the *Clanny* pattern (Fig. 194) is an example. The flame of the lamp is enclosed in a cylinder of wire gauze, so that when the lamp is placed in an explosive atmosphere the gases which penetrate to the flame are ignited and burn *inside* the gauze with a peculiar flickering, but the flame produced is unable to extend outwards through the gauze, unless the gauze becomes hot. The explosion which would be produced by a naked flame is thus averted. As soon as a miner notices the presence of the "fire-damp" flame, he leaves the working at once, and the mine is ventilated thoroughly. It has been found, however, that the Davy lamp is not an efficient protection against explosions in mines in all cases: thus a sudden and loud noise in the vicinity may so compress the air that the blue fire-damp flame inside may be quickly forced through the gauze to the outside, and the mixture outside may be ignited.

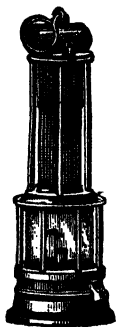


FIG. 194.

### 3. The Stationary and Variable States During Conduction

Suppose a bar of metal is placed with one end in a fire, and consider what takes place as the heat is transmitted outwards from the fire, along the length of the bar. The portion in the fire increases in temperature rapidly, and finally takes the temperature of the fire; meanwhile, as the temperature of this portion rises, the transverse layer adjacent to it receives heat by conduction, absorbs part of this heat to increase its own temperature, loses a small portion by radiation from its surface, and passes on the remainder to the next adjacent layer, where the process is repeated. When this has continued for some time, a state will be reached ultimately when each layer attains a stationary temperature and ceases to absorb any of the heat passed on to it by the adjacent layer nearer the fire.

This state has been called the **stationary or permanent state**, and the passage of heat along the bar, when this state is attained, depends, for given conditions, on the thermal conductivity of the material of the bar. The stage previous to the attainment of this stationary or permanent state is known as the **variable state**, because while it lasts each layer *absorbs* some portion of the heat it receives, and consequently is rising in temperature.

During the stationary state, each layer passes on to the next *less* heat than it receives by the amount which it loses by radiation from its outer surface. Hence, if there is any considerable loss of heat from the outer surface, the quantity of heat which passes from layer to layer decreases rapidly, and, at a comparatively short distance from the source of heat, the flow of heat along the bar becomes negligibly small. Therefore it is evident that in comparing the thermal conductivities of different substances by comparing the flow of heat along similar bars of these substances the bars must be not only similar in shape and dimensions, but the nature of the outer surfaces must be also exactly the same for each bar.

### 4. Definition of Thermal Conductivity

In all cases of thermal conduction the rate of transmission of heat—that is, the quantity of heat transmitted per second—in any direction, is found to depend upon the fall of temperature per unit distance in that direction. This *fall of temperature per unit distance* in any direction is called the gradient of temperature for that direction. The gradient of temperature for any direction may vary from point to point along that direction, and it is measured at any

point by the average gradient over a very short distance taken at the point. For example, in the case of a bar heated at one end, the gradient of temperature along the length of the bar decreases from point to point as the distance from the hot end increases. Also, if in a certain portion of the bar there is a fall of temperature of  $3^{\circ}\text{C}$ . in 2 mm., the gradient of temperature at the middle of this length of 2 mm. is  $15^{\circ}\text{C}$ . per cm.

Now imagine a large plate or wall of any substance, with parallel faces which are maintained at constant temperatures differing by a definite known amount, and consider the conduction of heat during the *stationary* state through the thickness of this wall from one face to the other. Near the edges of the plate some heat flows laterally outwards and escapes from the edges, but if a small portion of the plate near the centre and at a distance from the edges is considered, it may be assumed that all the heat which enters over any small area on the hot face of the plate passes through, *without lateral loss*, and emerges from the corresponding equal area on the cold face.

Under these conditions the quantity of heat which crosses any area of the plate depends on (1) the substance of the plate, (2) the area across which the flow of heat takes place, (3) the *gradient of temperature* in the plate—that is, the *difference of temperature per unit thickness* of the plate, (4) the time for which the flow of heat is taken. For a given substance, the flow of heat through the plate is directly proportional to (1) the area across which the flow takes place, (2) the gradient of temperature in the plate, (3) the time of flow. Therefore, the quantity of heat which flows in *unit time* through *unit area* of a plate in which there is a *gradient of temperature of one degree per unit thickness* depends only on the substance of the plate, and may be taken as a measure of the thermal conductivity of the substance. Thus the thermal conductivity of a substance is measured by the quantity of heat which flows in unit time across unit area of a plate of unit thickness having one degree difference between the temperatures of its faces. Thermal conductivity defined in this way is sometimes called the **absolute thermal conductivity** of the substance.

For the purpose of calculation it is convenient to put the statements given above in algebraical form. Let  $A$  denote the area,  $t$  the *difference* between the temperatures of the faces,  $x$  the thickness of the plate, and  $T$  the time of flow; then, since  $\frac{t}{x}$  is the gradient of

temperature for the direction of flow, if  $Q$  denotes the quantity of heat which passes through the area  $A$  of the plate in time  $T$ ,

$Q$  is directly proportional to  $A \cdot \frac{t}{x} \cdot T$ ;

$$\therefore Q = K \cdot A \cdot \frac{t}{x} \cdot T,$$

where  $K$  is a constant which measures the *absolute thermal conductivity* of the substance of the plate. This relation may be written

$$Q = KA \cdot G \cdot T,$$

where  $G$  is the temperature gradient. (If  $A = 1$ ,  $t/x$  or  $G = 1$ , and  $T = 1$ , then  $Q = K$ , as stated in the above definition.) In applying this relation any *consistent* set of units may be adopted. The system in most general use is the *c.g.s.* system, in which  $A$  is in sq. cm.,  $x$  in cm.,  $T$  in sec.,  $t$  in degrees C., and  $Q$  in calories.

**Example.**—It is found that the temperature of the rocks below the earth's surface increases at the approximate rate of  $1^\circ \text{C.}$  for each 30 m. descent. Taking the thermal conductivity of the rocks as 0.005 *c.g.s.* units, find how much ice will be melted by the heat arriving in the course of a year at 1 sq. m. of the earth's surface from its interior.

$$A = 1 \text{ sq. m.} = 10,000 \text{ sq. cm.,}$$

$$G = \frac{1}{30}^\circ \text{C. per m.} = \frac{1}{3000}^\circ \text{C. per cm.,}$$

$$T = 1 \text{ yr.} = 365 \times 24 \times 60 \times 60 \text{ sec.}$$

Hence, the quantity of heat arriving per square metre of surface per year is given by—

$$Q = 0.005 \times 10,000 \times \frac{1}{3000} \times 365 \times 24 \times 60 \times 60 \text{ calories.}$$

The latent heat of fusion of ice is 80 calories per gm. Therefore—

$$\text{Mass of ice melted} = \frac{50 \times 365 \times 24 \times 60 \times 60}{3000 \times 80} = 6570 \text{ gm.}$$

This mass corresponds to a layer of ice 0.7 cm. in thickness.

## 5. Influence of Specific Heat During Conduction

The rate at which heat is conducted through any substance, during the *variable* state, depends not only upon the thermal conductivity of the substance, but also upon its specific heat and density. The product of these is the quantity of heat required to raise the temperature of unit volume by  $1^\circ \text{C.}$ , or the specific heat per unit volume (page 115). If this product is small, the temperatures of the successive layers rise quickly to the stationary points, even when the thermal conductivity is comparatively low, for only a small portion of the heat which travels along is required to heat

the substance. Similarly, if the specific heat per unit volume is high, the temperatures of the successive layers may rise slowly to the stationary values, even when the conductivity of the substance is fairly high. This is illustrated by the following experiment:—

*Experiment.* Place two bars of iron and bismuth, of the same size and shape, and having exactly similar surfaces, end to end (Fig. 195). To the under surfaces attach with wax small wooden balls, at equal distances along the lengths of the bars, and heat the bars at their contiguous ends. As the heat is transmitted along the bars, the wax melts and the balls drop off in succession. The first ball will drop off directly the temperature of the point at which it is attached becomes equal to the melting point of wax, and, provided that the distance of this point from the source of heat be not too great, the time required for this to take place depends not mainly upon the thermal conductivity, but on the specific heat of the

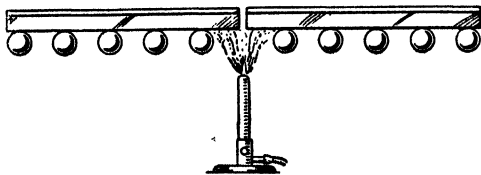


FIG. 195.

material of the bar; because, the lower the specific heat of this material, the greater will be the rise of temperature produced in a given volume of it by the heat supplied in a given time. For

this reason the balls begin to drop off first from the bismuth bar, for the specific heat of bismuth is much less than that of iron; but ultimately the greater number of balls will drop off from the iron bar, for the thermal conductivity of iron is much greater than that of bismuth, and, the greater the flow of heat along the bar, the further will the rise of temperature necessary to melt the wax be transmitted.

## 6. Diffusivity or Thermometric Conductivity

It is necessary sometimes to consider the effect of a flow of heat in producing change of temperature in the portion of the material from or to which the flow takes place. In such cases it is convenient to express the *quantity of heat transmitted* in terms of the specific heat per unit volume of the substance in which the flow takes place. If the specific heat of unit mass of a given substance is denoted by  $s$ , and its density by  $d$ , the specific heat per unit volume is given by  $sd$ . If  $K$  denotes the absolute thermal conductivity of this substance, then the flow of heat, in unit time, across a unit cube of

the substance, having unit difference of temperature between its opposite faces, is expressed *in the usual thermal units* by  $K$ , but, *if the specific heat per unit volume of the substance be taken as the unit of heat*, this flow of heat is expressed by  $\frac{K}{sd}$ .

This method of considering the flow of heat is analogous to that adopted in studying the diffusion of liquids and gases, and the quantity  $\frac{K}{sd}$  has been termed the **diffusivity** of the substance by *Kelvin*, and may be considered as the coefficient of diffusion of heat, denoted by  $k$ . The diffusivity of any substance evidently may be measured by the rise of temperature, produced in a layer of that substance of unit thickness, by the heat transmitted in unit time through a similar layer of unit thickness, having unit difference of temperature between its faces. For this reason diffusivity has been called **thermometric conductivity** by *Maxwell*, as opposed to *absolute conductivity*, which for a similar reason has been termed **calorimetric conductivity**.

From what has been said above it will be understood that, during the *variable* state, when the specific heat of the substance has an influence on the result, the transmission of heat is related to *diffusivity*, whereas, when the *stationary* state is attained, only *conductivity* is involved. For this reason, comparative determinations of the thermal conductivities of substances of different specific heat should be made from data furnished by observations made during the *stationary* state.

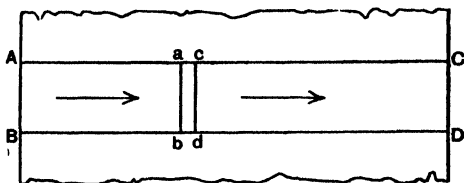


FIG. 196.

## 7. Flow of Heat Across a Section Perpendicular to the Flow

Consider the flow of heat through unit area of the plate mentioned above (Art. 4). Let ABCD (Fig. 196) represent a portion of the plate, having its ends, AB, CD, each of unit area, on the two faces of the plate and its sides, AC, BD, perpendicular to the faces of the plate and therefore parallel to the direction of flow of heat. Now consider a thin layer,  $abcd$ , having its faces,  $ab$ ,  $cd$ , perpendicular to AC, BD. Then, when the stationary state is reached, the flow of heat through this layer is constant wherever it lies in the thickness



of the plate, because, as its temperature is constant, as much heat must be passing out through  $cd$  as flows in through  $ab$ , assuming that there is no lateral loss of heat.

Let  $Q$  = flow of heat in unit time through layer,  $abcd$ ,

$t$  = difference of temperature between the faces,  $ab$ ,  $cd$ ,

$x$  = the distance between the faces,  $ab$ ,  $cd$ .

$$\text{Then, } Q = K \cdot \frac{t}{x}. \quad (\text{Art. 4.})$$

The application of this relation involves the assumption, first made by *Fourier*, that, within very narrow limits, the flow of heat is proportional to the difference of temperature. Starting with this assumption, and the more general one that  $Q$  is some function of  $x$ , it can be shown that, under the conditions here considered,  $Q \propto \frac{t}{x}$ ; so that the result, though assumed here and in Art. 4, is not essentially an assumption. The general assumption referred to has been proved, by indirect experiment, to be correct.

But  $Q$  is constant, and so also is  $K$  in the majority of substances, therefore  $\frac{t}{x}$  must be constant. This means that *the temperature gradient is uniform*. Hence, in the case of a steady flow of heat with uniform temperature gradient, the flow across any section in unit time is given by

$$Q = K \cdot \frac{t}{x},$$

where  $t$  now denotes the difference of temperature between *any* two sections, taken perpendicular to the direction of flow and separated by a distance,  $x$ . That is, if  $t_1$  and  $t_2$  are the temperatures of the two faces,  $AB$ ,  $CD$ , of the plate (Fig. 196),

$$Q = K \cdot \frac{t_1 - t_2}{AC}.$$

A flow of heat of this nature, however, is met with rarely, for it involves the condition that there is no lateral loss of heat; that is, loss of heat through  $ac$ ,  $bd$ . In cases of conduction, such as the flow of heat along a bar heated at one end, there is considerable lateral loss of heat by radiation and convection from the surface of the bar. Thus the heat passing through any cross-section of the bar is less and less the further that section is taken from the

heated end of the bar. Therefore, the temperature gradient is not uniform and the result obtained above is not applicable.

Let  $XY$  (Fig. 197) represent the bar considered of unit cross section, and  $abcd$  a layer of very small thickness,  $\delta$ , having a very small difference of temperature,  $\tau$ , between its faces. Then, if  $\tau$  and  $\delta$  are small enough, the temperature gradient in this layer may be considered uniform, and, as above

$$Q = K \cdot \frac{\tau}{\delta}.$$

If now the face  $cd$  be made to approach  $ab$  until  $\delta$ , and consequently also  $\tau$ , become infinitesimally small, the lateral loss diminishes, and ultimately the flow of heat across the layer becomes the flow across the section  $ab$ , and

$$Q = K.G,$$

where  $G$  is the value of the temperature gradient at  $ab$ —that is, the limit of the ratio  $\frac{\tau}{\delta}$ , when both  $\tau$  and  $\delta$  vanish simultaneously.

Thus is obtained the result:—

$$\left\{ \begin{array}{c} \text{Flow of heat across} \\ \text{any section} \end{array} \right\} = \text{Conductivity} \times \left\{ \begin{array}{c} \text{Value of temp. gradient} \\ \text{at that section} \end{array} \right\}$$

The above problems lend themselves to graphical treatment. In the first case, the graph between temperature and distance may be represented by the straight line (Fig. 198) obtained by drawing ordinates at  $A$  and  $C$  equal to  $t_1$  and  $t_2$ , and joining them. The temperatures at any intermediate points, such as  $a$  and  $c$ , may be obtained by drawing ordinates  $aP$ ,  $cQ$ , at  $a$  and  $c$ , to meet this line.

In this case it is evident that  $\frac{t}{x}$  for any little slab,  $abcd$ , is equal to

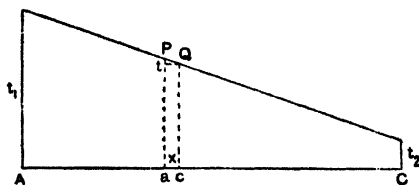


FIG. 198.

$$\frac{aP - cQ}{ac} = \frac{t_1 - t_2}{AC}, \text{—that is,}$$

the temperature gradient is the same at all points along  $AC$ , and equal to the tangent of the angle the straight line makes with  $AC$ .

In the second case, suppose that the temperatures at X and Y are  $t_1$  and  $t_2$  as before. The temperature graph now is not a straight line, but a curve. The exact form of this curve can be obtained only by experiment, but is usually somewhat of the shape shown (Fig. 199). Draw ordinates,  $aP$ ,  $cQ$ , to cut this curve and join  $PQ$ . Let  $\alpha$  be the inclination of  $PQ$  to  $XY$ . The ratio

$$\frac{\tau}{\delta} = \frac{aP - cQ}{ac} = \tan \alpha,$$

and when  $\tau$  and  $\delta$  vanish simultaneously, the ratio,  $\frac{\tau}{\delta}$  becomes equal to the tangent of the angle the tangent to the curve at P makes with  $XY$ —that is, the temperature gradient at any point of the bar is given by the tangent of slope of the temperature curve at that point.

### 8. Determination of Absolute Thermal Conductivity

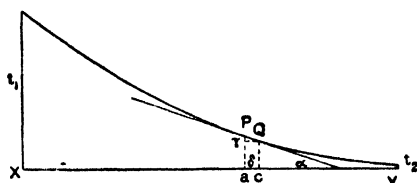


FIG. 199.

Theoretically, it would appear that the simplest method of determining the absolute conductivity of a substance would be to measure the quantity of heat transmitted through a plate of the substance of known area and thickness,

and having a known difference of temperature between its faces, and then to apply the relation,  $Q = K.A.\frac{t}{x}.T$  (Art. 4). This method, however, does not give accurate results because (1) it is difficult, if not impossible, to maintain the two faces at constant *known* temperatures, (2) it is impossible to avoid *lateral* losses of heat by radiation and convection from the edges of the plate.

On this account, the most usual method of investigating thermal conductivity in the case of a metal is to take a bar of the metal the conductivity of which is to be determined, and, keeping one end at a high constant temperature, to note the temperature assumed at different points in its length when the stationary state is attained. **Forbes** was the first to conduct an investigation of this nature in such a way as to obtain results entirely dependent on experimental observations. In these experiments, the bar, AB (Fig. 200), had one extremity, A, fixed in a vessel of molten lead, and was of such

length that the temperature of the other extremity, B, was unaffected by the source of heat at A. The screen, SS, served to protect the bar from radiation from the molten lead. To determine the temperatures at different points in the length of the bar, small holes were drilled into it at equal distances apart, and, after partly filling them with mercury, the bulbs of small thermometers were inserted; the reading of each thermometer then gave the temperature of the bar at the centre of the hole in which it was inserted. A better method of taking the temperatures is to apply a calibrated thermocouple (page 30) to each part of the rod in turn. Great precautions were taken to keep the end, A, at a constant temperature, and when the stationary state was attained, as shown by the steady readings of the thermometers placed along the bar, these readings were observed carefully and recorded.

From the data thus obtained a temperature-distance graph was plotted, and from the curve it was possible to determine the temperature at *any* point on the bar, and by drawing tangents to the curve to determine, as explained above (Art. 7), the temperature gradient at any point. Thus, one factor,  $G$ , of the relation,  $Q = KG$ , was determined.

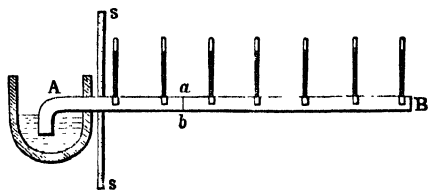


FIG. 200.

If, now,  $Q$  can be determined,  $K$  can be calculated. Consider what becomes of the heat which flows past the section,  $ab$ , of the bar, AB (Fig. 200). The stationary state having been attained, there is no absorption of heat at any point, and consequently it must follow that all the heat passing through  $ab$  must be lost by radiation and convection from the surface of the bar beyond  $ab$ —that is, from the surface of the portion  $aB$ . If, then, the amount of this radiation and convection from each element of the bar beyond  $ab$  can be determined, the sum total of this loss of heat will represent the flow across  $ab$ .

To make this determination, Forbes heated a short bar, similar to AB in all respects except length, to a temperature equal to the highest observed temperature on AB, and then observed carefully the rate of cooling. It has been shown (page 120) how loss of heat can be estimated from rate of cooling if the specific heat of the substance cooling is known, and Forbes deduced in this way the

heat lost by radiation and convection per second from a unit length of the bar for any given excess temperature—that is, temperature difference between this unit length of bar and the surrounding air. By adding the amounts of heat lost in this way for each unit length of bar beyond the section, *ab*, the total quantity of heat which has crossed the section, *ab*—that is,  $Q$ —is obtained. Having obtained  $G$  and  $Q$ ,  $K$  can now be calculated from the relation,  $Q = K \cdot G$ .

It should be noticed that a large number of determinations can be made from the data of the experiment, for the flow of heat across any number of sections may be considered. Further, since each section is at a definite *known* temperature, the value of  $K$  obtained for any section gives the thermal conductivity of the material of the bar *at that temperature*, and consequently this method of observation serves to determine whether  $K$  varies with the temperature, or is constant. Forbes found that in the case of iron the thermal conductivity decreases with increase of temperature—that is, hot iron does not conduct so well as cold iron.

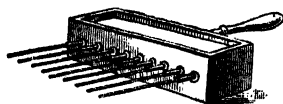


FIG. 201.

If the thermal conductivity of the material of the bar is the same at all temperatures, it may be shown mathematically that if the distances of a series of points from the constant high temperature end increase in arithmetical progression, the excess temperature of the bar at these points decreases in geometrical progression.

## 9. Determination of Relative Thermal Conductivity

Forbes' method has been employed to determine the relative thermal conductivities of different metals. The method of reducing the observations is beyond the scope of this book. In all such methods, however, two things must be attended to carefully—(1) the observations must be made during the stationary state (see Art. 5, and page 319), (2) the surfaces of the bars must be of the same extent and nature. This latter condition is of equal importance with the first, for the fall of temperature along a bar evidently depends on the rate of loss of heat from the surface; and this depends on the nature and extent of that surface. **Wiedemann and Franz**, in their experiments on relative conductivity by this method, employed thin rods of the same size and shape, and electro-plated their surfaces to ensure exact similarity in their nature.

Rough determinations of the relative conductivities of different substances may be made by means of an apparatus due to *Ingen Hausz*. This consists of a box (Fig. 201) into which rods of different metals of the same diameter are fixed, as shown. The ends of the rods pass into the box, and are raised to a constant high temperature by filling the box with hot water or oil and heating with a Bunsen burner. The front plate of the box is made of thick copper, and the rods should be made to fit exactly, without corks, into holes drilled in this plate. The portions of the rods outside the box are coated with wax, so that, as heat is transmitted along their lengths, the wax gradually melts. The rods should be of such a length that the outside ends are at the temperature of the surrounding air, and the rods should be protected from direct heating by means of a screen which, in some forms of the apparatus, is attached to the box. Instead of coating the rods with wax, it is more satisfactory to place the wax in a narrow longitudinal groove running the whole length of each rod. The greater part of the surface of each rod can then be polished, or electro-plated, so as to ensure exact similarity of surface. When the stationary state is attained, the relative lengths along which the wax melts depend on the thermal conductivities of the metals used.

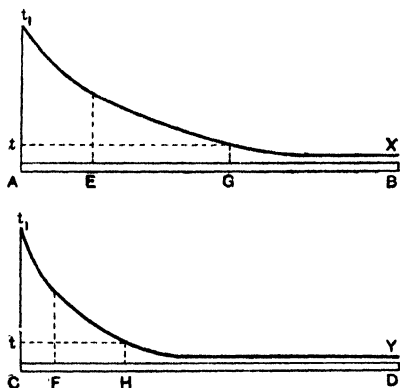


FIG. 202.

To deduce the relative values of the thermal conductivities from the lengths of the rods along which the wax has melted, consider two rods, AB and CD (Fig. 202), along which the wax has melted distances, AG and CH respectively. Assume, for the sake of simplicity, that AG is twice CH. If  $t_1$  is the temperature of the hot bath and  $t$  that of the melting point of wax, the temperature curves will be as shown, the equal ordinates at X and Y representing the temperature of the air surrounding the rods.

Take a cross-section at any point, E, on AB, and find the section at F on CD which has the same temperature. Then, it is evident that  $AE = 2CF$ , and  $EG = 2FH$ , and, in general, that the length

of any portion of the rod, AB, is always twice the length of the portion of the rod, CD, having its ends at the same two temperatures. Since the heat passing along a rod across any section is lost by radiation and convection from the surface of the portion of the rod beyond that section, it follows that the quantity of heat which crosses the section at E of AB in a given time is twice the quantity of heat which crosses the section at F of CD in the same time.

Again, since  $AG = 2CH$ , the temperature gradient at any section of AB is always half that at the section of CD at the same temperature—that is, the temperature gradient at E is half that at F. Now apply the relation of Art. 4: then:—

$$Q_1 = K_1 A_1 G_1 T, \text{ for AB,}$$

$$Q_2 = K_2 A_2 G_2 T, \text{ for CD.}$$

Now  $A_1 = A_2$ , and  $T$  is the same for each rod; therefore—

$$\frac{Q_1}{Q_2} = \frac{K_1}{K_2} \cdot \frac{G_1}{G_2}.$$

But,  $Q_1 = 2Q_2$ , and  $G_1 = \frac{1}{2}G_2$ ; hence,

$$2 = \frac{K_1}{K_2} \cdot \frac{1}{2}, \quad \therefore \frac{K_1}{K_2} = 2^2,$$

that is, the thermal conductivity of the material of the rod, AB, is four times that of the material of the rod, CD.

The above proof may be made quite general. If the length of the wax melted along AB is  $n$  times that of the wax melted on CD, then  $Q_1 = nQ_2$ , and  $G_1 = \frac{1}{n}G_2$ , and therefore

$$\frac{K_1}{K_2} = n^2,$$

that is, the thermal conductivities are proportional to the squares of the lengths along which the wax has melted.

**Example.**—In such an experiment, the lengths of the rods along which the wax melted were 10.0 cm. for copper, 5.6 cm. for brass, and 4.0 cm. for steel. Compare the thermal conductivities of the metals.

$$K_1 : K_2 : K_3 :: 10.0^2 : 5.6^2 : 4.0^2,$$

or,  $K_1 : K_2 : K_3 :: 100 : 31.36 : 16.$

It may be remarked here that, if the metals are arranged in the order of their thermal conductivities and also in the order of their *electrical* conductivities, the two lists will be found to contain the

metals in much the same order, thus showing a close connexion between thermal and electrical conductivities.

## 10. Laboratory Determinations of the Thermal Conductivities of Solids

The method to be adopted for the determination of the thermal conductivity of a solid depends upon whether the substance is a good conductor or a poor conductor, and also upon the form in which the substance is available. Numerous methods and forms of apparatus have been devised for experimental work on thermal conduction in the laboratory, and a selection of these will now be described.

(I) SEARLE'S APPARATUS.—This apparatus is suitable for the determination of the thermal conductivity of a metal, such as copper, which can be obtained in the form of a solid bar. The principle of the method of use is based on *Forbes' method* (Art. 8) and a modification of it used by *Callendar and Nicholson*.

The bar of metal, about 5 cm. in diameter and 20 cm. in length, is fitted at one end into a cylindrical chamber, A (Fig. 203), through which steam can be passed. Near the other end of the bar, a spiral of thin copper tubing, B, is fixed on the bar, and fitted so that a stream of cold water may be passed through the tube, the temperature of the water as it enters and leaves the tube being indicated by thermometers,  $T_3$  and  $T_4$ . Holes are drilled in the bar at C and D, a known distance apart, and thermometers,  $T_1$  and  $T_2$ , are placed in copper tubes fixed in these holes. The whole bar and its attached fittings are surrounded with layers of thick felt and packed in a strong wooden case, which prevents any appreciable loss of heat from the bar except that given to the water in B.

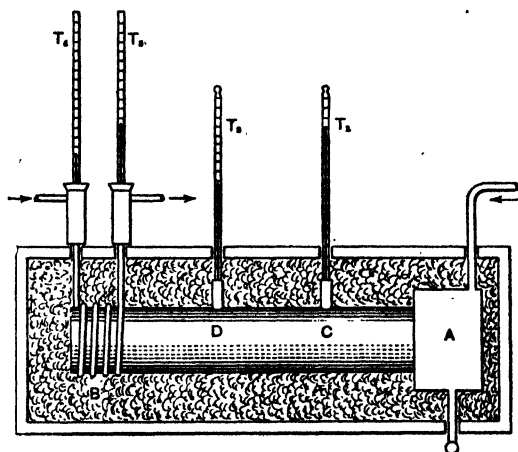


FIG. 203.



To use the apparatus, steam is passed through the chamber, A, and a steady stream of cold water through the spiral, B, the rate of flow being kept steady by means of a constant head apparatus (see Fig. 154). Heat is thus communicated to the bar, the felt prevents any appreciable loss from the surface of the bar, and the heat passes to the circulating water. The stationary state is attained when the flow of heat through the bar is equal to that received by the water, and a temperature gradient is established in the bar. The quantity of heat,  $Q$ , is obtained by finding the mass of water,  $M$ , passing through the spiral in a given time,  $T$ , and noting the temperatures,  $t_3$  and  $t_4$ , indicated by the thermometers,  $T_3$  and  $T_4$ . The temperature gradient is obtained by noting the

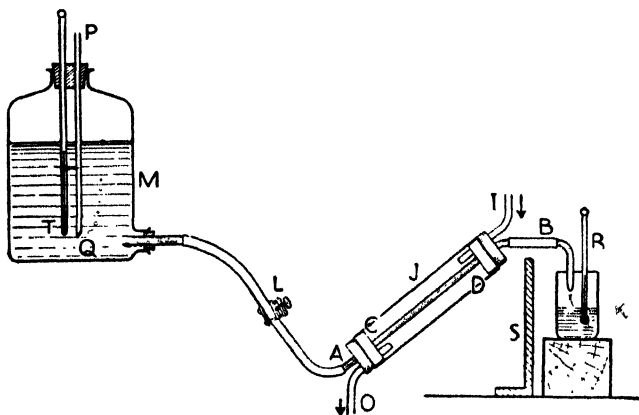


FIG. 204.

temperatures,  $t_1$  and  $t_2$ , indicated by the thermometers,  $T_1$  and  $T_2$ , and their distance,  $x$  cm., apart. The area of cross-section,  $A$ , of the bar is obtained by measurement of the diameter of the bar. Then, using the relation (Art. 4),  $Q = K.A.G.T$ , it is seen that

$$M(t_3 - t_4) = K.A.\frac{t_1 - t_2}{x}.T,$$

from which  $K$  can be calculated. In carrying out an experiment, it is essential to wait until the readings of all four thermometers are constant.

(2) **PECLET'S METHOD.**—This method is suitable for the determination of the thermal conductivity of a poor conductor, such as

glass or porcelain, which can be obtained in the form of a tube. AB (Fig. 204) is the tube of material whose thermal conductivity is required. A certain length of it, CD, is fixed in a jacket tube, J, through which steam can be passed. M is a Mariotte's bottle containing water, and fitted with a thermometer, T, and a tube, PQ, open at P. When the screw clip, L, is opened, air bubbles through PQ so that, whatever the quantity of water in M, a constant rate of flow is maintained. After passing through the tube, AB, the water is collected in a beaker, K, in which a thermometer, R, is suspended. The beaker and its contents are screened from the steam jacket by S.

When steam is passed through the jacket, J, heat flows through the walls of the tube, CD, and is communicated to the water. When the stationary state is attained, the quantity of heat, Q, is obtained by observing the mass, M, of water collected in the beaker, K, in a given time, T, and the temperatures,  $t_1$  and  $t_2$ , indicated by the thermometers, T and R. Then:—

$$Q = M (t_2 - t_1).$$

The average temperature of the water flowing through CD is given by  $(t_1 + t_2)/2$ . Hence, if the external and internal radii of the tube are  $r_1$  and  $r_2$ , the temperature gradient, G, is given by—

$$\frac{\left(100 - \frac{t_1 + t_2}{2}\right)}{r_1 - r_2},$$

assuming the temperature of the steam to be  $100^\circ \text{C}$ . The external radius,  $r_1$ , is found by measuring the diameter of the tube by means of calipers, readings being taken at several different places. The internal radius,  $r_2$ , is found by weighing the quantity of water required to fill a measured length of the tube. Also, since the flow of heat is radial, the area, A, exposed to the heat, if the wall of the tube is thin, may be taken as the mean between the areas of the external and internal surfaces—that is,  $A = 2\pi \left(\frac{r_1 + r_2}{2}\right) l$ , where  $l$  is the length, CD, of the tube. Thus, using the relation (Art. 4),  $Q = K.A.G.T$ , we get:—

$$M (t_2 - t_1) = K \cdot \pi \left(\frac{r_1 + r_2}{2}\right) l \cdot \frac{\left(100 - \frac{t_1 + t_2}{2}\right)}{r_1 - r_2} \cdot T,$$

from which K can be calculated.

If the wall of the tube is thick, so that the ratio,  $r_1/r_2$ , is very far from unity, the more correct relation is:—

$$M(t_2 - t_1) = \frac{2\pi K l T \left(100 - \frac{t_1 + t_2}{2}\right)}{\log_e \frac{r_1}{r_2}}.$$

This method may be modified to determine the thermal conductivity of india-rubber. A piece of ordinary thick-walled pressure tubing, through which steam may be passed, is used, and a measured length of this tubing is immersed in water contained in a calorimeter. The heat transmitted through the walls of the tubing is determined from the mass of water in the calorimeter and the rate of rise of temperature of the water.

(3) LEES' AND CHORLTON'S METHOD.—This method is suitable for the determination of the thermal conductivity of a poor conductor, such as ebonite or cardboard, which can be obtained in the form of a thin disc. The apparatus is based on that used by Lees in an extensive research on the thermal conductivities of

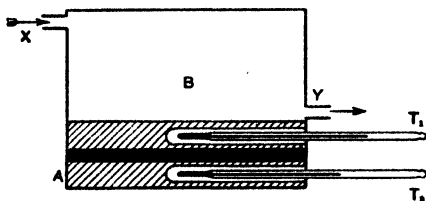


FIG. 205.

various substances, both solid and liquid.

A disc of brass, A (Fig. 205), is supported by means of strings from a large ring on a retort stand. The disc of the substance whose thermal conductivity is to be determined is placed on the brass disc, the diameter being equal to that of the brass. Then a hollow brass cylinder, B, of the same diameter and provided with side tubes, X and Y, is placed on the specimen. Mercury thermometers,  $T_2$  and  $T_1$ , are inserted in holes drilled in the plate, A, and the base of the cylinder, B. The surfaces of A and B are electroplated.

To use the apparatus, steam is passed through B until the stationary state is attained, when the temperatures indicated by the thermometers remain steady. Heat is conducted through the specimen, and the stationary state is attained when the rate of flow of heat is equal to the rate at which the heat is lost from the surfaces of the plate, A. The temperatures are noted and the area

of cross-section and the thickness of the specimen are found by measurement. To determine the rate of flow of heat, the plate, A, is raised to a temperature higher than that indicated by the thermometer,  $T_2$ , and allowed to cool in the same conditions as during the first part of the experiment, the temperature being noted at regular intervals of time. A graph is then plotted and from the cooling curve obtained, the rate of cooling of the plate, at the temperature indicated by the thermometer,  $T_2$ , in the stationary state, is found by drawing a tangent to the curve at the point representing this temperature.

If A denotes the area of cross-section of the specimen,  $d$  its thickness,  $t_1$  and  $t_2$  the temperatures indicated by the thermometers in the stationary state, then (Art. 4)

$$Q = K.A.G.T = K.A.\frac{t_1 - t_2}{d}.T;$$

$$\therefore \frac{Q}{T} = K.A.\frac{t_1 - t_2}{d}.$$

If M is the mass of the plate, A,  $s$  the specific heat of the metal, and  $t$  the rate of cooling per second obtained in the second part of the experiment, then

$$\frac{Q}{T} = Mst; \therefore Mst = K.A.\frac{t_1 - t_2}{d},$$

from which K can be calculated.

## 11. The Thermal Conductivity of Liquids

The thermal conductivities of all liquids, except mercury and other liquid metals, are very small. For this reason it is difficult to exhibit thermal conduction in a liquid experimentally, and the difficulty is increased by the influence of convection currents and by the conduction of heat through the walls of the necessary containing vessel. However, if a liquid is heated from *above*, convection currents are not produced, and the conduction through the walls of the containing vessel may be made negligibly small by using thin-walled vessels of badly conducting material. The following experiment illustrates the small conductivity of liquids.

*Experiment.* Load a piece of ice by twisting a piece of thick copper wire round it, and place it in a large test-tube nearly full of

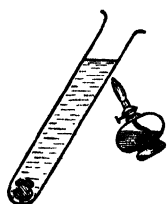


FIG. 206.

water (Fig. 206). Fix the tube in an inclined position on a retort stand, and heat it near the top by a spirit lamp or Bunsen burner. It will be found that the water at the top will boil before much of the ice is melted.

The thermal conductivity of water was investigated by **Despretz** by a method similar to that used by **Forbes** for rods of metal (Art. 8). The essential parts of the apparatus used are shown (Fig. 207). ABCD is a large wooden cylinder containing water and having thermometers fitted through the walls. A current of hot water at constant temperature was passed through the metal pan, PP, which rested on the surface of the water in ABCD. After an interval of more than 24 hours it was found that the stationary state had been attained. The rest of the experiment was then carried out as in **Forbes'** method.

A somewhat similar method was used by **Berget** to determine the thermal conductivity of mercury. The mercury was contained in a glass tube, AB (Fig. 208), the lower end of which formed part of a Bunsen ice calorimeter (page 142). The upper part of the mercury column was surrounded by another column of mercury, which prevented loss of heat by lateral radiation from the central column. The mercury was heated at the upper surface by steam passing through tubes as shown. When the stationary state was attained, the temperatures at four places, 1, 2, 3, 4, were measured by thermoelectric junctions (page 30) which consisted of iron wires inserted in the mercury through holes pierced in the walls of the tube. The quantity of heat flowing through the mercury column, AB, was determined from the amount of ice melted on the lower part of the tube in the Bunsen ice calorimeter.

## 12. The Thermal Conductivity of Gases

The thermal conductivities of gases are extremely small. In a mass of gas uniformity of temperature is established more quickly by convection than in a mass of good conducting material by conduction. The very low conductivity of cotton-wool, eiderdown, felt, and other fabrics of open texture is due very largely to the air enclosed in the fabrics.

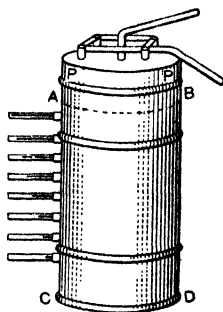


FIG. 207.

In the determination of the thermal conductivity of a gas the difficulties referred to above for liquids (Art. 11) are met with to such a degree that the determination is extremely difficult. Indirect determinations have been made, however, from observations of the rate of cooling of a body in a gas under such conditions as to eliminate the effects of convection. It is now a familiar fact that the cooling of a body depends on the thermal conductivity of the substance surrounding it, and hence it will be understood that the rates of cooling of a hot body, *in vacuo*, and when surrounded by a gas, will be different, and that, if convection have no effect on the result, this difference will depend on the thermal conductivity of the gas. When the pressure of the gas is reduced to a certain value, it is found that the effects of convection currents become very small. For this reason, observations on the rate of cooling of a hot body in a suitable enclosure were made when the body was surrounded by the gas under investigation at a pressure of about 150 mm. or less.

By such indirect determinations it was found that the thermal conductivity of hydrogen was about seven times that of air.

**Experiment.** Fit a piece of platinum wire about 20 cm. long into a wide glass tube (Fig. 209). Exhaust the tube and pass an electric current through the wire, adjusting the strength of the current until the wire glows

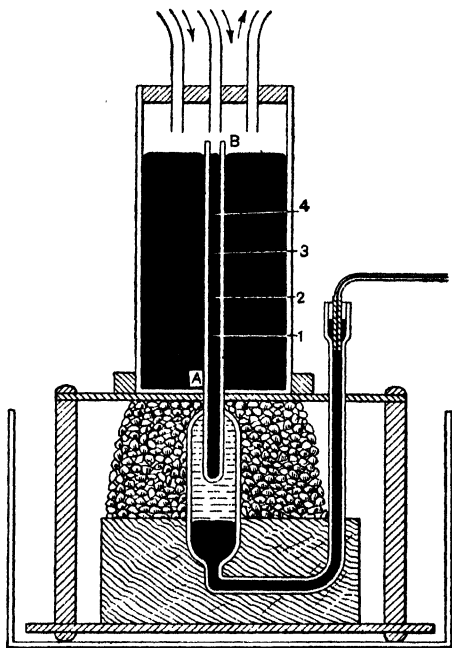


FIG. 208.

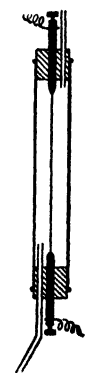


FIG. 209.

brightly. Now admit air into the tube and pass the same current. The glow is less bright, showing that the heat is being conducted away from the wire by the air. Again exhaust the tube and fill with hydrogen. Again pass the same current. The wire does not glow at all, thus showing that hydrogen is a much better conductor of heat than air.

Recent determinations of the thermal conductivities of gases have used the principle indicated by the above experiment. A thin platinum wire is sealed in a glass tube containing the gas under investigation, the tube being immersed in an ice-bath to maintain a constant temperature. An electric current is passed through the wire, its temperature is raised and heat is conducted through the gas to the walls of the tube. When the stationary state is attained, the strength of the electric current is observed and the resistance of the platinum wire is measured. From these observations the quantity of heat developed is calculated, and from the latter the temperature of the wire is found in the same manner as in the case of a platinum resistance thermometer (page 25). The effects of convection currents in the gas are eliminated by reducing the pressure of the gas in the tube, and corrections are calculated for the loss of heat by radiation from the wire and for the conduction of heat through the glass walls of the tube.

## CHAPTER XVII

### RADIATION

AS already mentioned (page 307), radiation is different from conduction and convection. Heat is said to pass by radiation when it is transmitted from one body to another, through a vacuum, or through an intervening material medium *without affecting the temperature of the medium*. The heat of the sun reaches the earth by radiation, as does also the warmth experienced when standing before a fire. A thermometer suspended in a vessel from which the air has been exhausted receives heat from external objects; this shows that the presence of air is not necessary to the passage of heat by radiation. Again, a piece of black cloth, if exposed to the rays of the sun on a frosty day, becomes much warmer than the surrounding air; this shows that heat passes through a medium like air without warming it nearly so much as it does some object in the medium or beyond it.

Other gases besides air have been found to allow readily the passage of heat by radiation. The drier a gas is the more readily does heat traverse it by radiation. Experiments have shown, however, that heat travels through a vacuum even better than through the driest gas.

Many solids and liquids allow radiation to pass through without being themselves warmed to any great extent: for example, rock salt and carbon bisulphide. Other bodies, such as wood, slate, metal, etc., do not permit the passage, but absorb the energy, and therefore become heated.

#### 1. Nature of Radiation

Various experiments have proved that radiation, or *radiant heat*, is transmitted in the same way as light. In the first place, most bodies which are transparent to light are more or less transparent to radiant heat. Again, the velocity with which heat is radiated from hot bodies is the same as that with which light travels from luminous bodies. During a total eclipse of the sun, for example, both heat and light are cut off simultaneously. Also, heat is reflected from polished surfaces, and the laws of its reflection are the same



as in the case of light. It is also refrangible, and thus can be brought to a focus by a lens; the use of a simple lens as a burning-glass shows that the heat which has passed through the lens is concentrated at about the same spot as the rays of light. Heat is radiated from one body to another through a vacuum, and light also is transmitted through a vacuum.

As the radiation of heat bears so many analogies to the passage of light, it has long been assumed that both are transmitted by a wave motion in the ether. (As already mentioned, some physicists now "ignore" ether and regard the ability to transmit these forces, this radiation, as being simply a property of "free space"—an ultimate fact of Nature.) As the term *rays of light* is used, so *rays of heat* may be referred to in a similar sense.

The molecules of a white-hot body are in a state of rapid vibration, the frequencies of vibration being very different for molecules of different substances and for the same molecules at different temperatures. These moving molecules are supposed to disturb the ether around them and send waves of disturbance through it. The velocity with which these waves travel through the ether is the same. All waves, whatever the frequency, heat bodies *when they are absorbed* by the bodies. The most familiar hot bodies, including the sun, send out most of their energy in vibrations of frequency too small to excite vision. If the body is black, such as lampblack, it absorbs all the incident radiation, and hence all the energy of the waves is spent in heating the body. The several properties of the waves which depend more or less upon the frequency are, however, described more fully in textbooks of Light (see Stewart and Satterly, *Textbook of Light*).

A better term for *radiant heat* is *radiant energy*. However, the term radiant heat will be used for waves of low frequency which do not excite vision. Another term used is *infra-red* rays, since these rays are refracted by a prism to a less extent than the visible red rays.

When a body is first heated, it sends out waves of low frequency, or long wave-length. As the heating is continued, waves of higher frequency or shorter wave-length are added to these until, when the temperature rises to about  $500^{\circ}\text{C.}$ , the waves added are quick enough to excite in the eye the sensation of red light. As the heating is continued still further, waves which excite the sensations of orange, yellow, green, blue, and violet light are added successively, so that the colour of the body changes gradually, the waves exciting the violet sensation being added at about  $1400^{\circ}\text{C.}$  The body now

appears white-hot. Further heating does not alter the colour, but enables the body to send out waves of very high frequency or very short wave-length which have intense chemical and electrical effects. These very high frequency waves are called *actinic* or *ultra-violet*; they are refracted by a prism more than the violet waves. All the waves carry energy, and have a claim to the title of radiant heat. However, this name is given specially to the infra-red waves because these carry the greater proportion of the heat emitted by such sources as a coal fire, and constitute the whole of the heat emitted by hot water, etc.: it is these which are dealt with in the present chapter.

It should be noted (as stated above) that the higher the frequency the less is the wave-length, and the lower the frequency the greater is the wave-length, for the product of the frequency and wave-length is numerically equal to the velocity which is constant, viz. 186,000 miles or 300,000,000 metres per second. Incidentally, "ether" waves of higher frequency than the actinic or ultra-violet waves include X-rays, gamma-rays (from radium and other radio-active bodies), and cosmic rays, whilst "wireless" waves are of much lower frequency than the infra-red to be dealt with in this chapter. All these ether waves, however, are of the same "general" character—they are all *electro-magnetic* waves. (See Hutchinson's *Advanced Textbook of Magnetism and Electricity*.)

## 2. The Behaviour of Bodies Towards Radiant Heat

When radiant heat is incident on the surface of any medium, it is, in general, split up into four parts:—

(1) A portion which suffers **regular reflection** at the surface of the medium in accordance with the ordinary laws of reflection.

(2) A portion which suffers *reflection* at minute irregular parts of the surface. This is called **diffusion**.

(3) A portion which is *refracted* into the medium in accordance with the laws of refraction. A part of this is (a) **transmitted** by the medium, and the remainder is (b) **absorbed** by the medium.

The theoretical relations between the quantities reflected, diffused, transmitted, and absorbed will be dealt with later (Art. 17). If the reflection, diffusion, transmission, and absorption of radiant heat be taken as established by experiment, it may be stated, without further experiment, that if any medium exhibit any one or more of these properties in a marked degree, it must exhibit the others in a proportionately smaller degree.

It is now the function of experiment to analyse each of the above phenomena. In so doing it is necessary, in each case, to determine, (1) the general laws of the phenomenon, (2) the properties of different media in relation to the phenomenon, (3) the influence of the surface of the medium, and (4) the influence of the nature of the source of heat from which the radiation takes place. The methods and results of experimental investigations carried out in this way will now be indicated briefly.

### 3. Instruments Used in Experiments on Radiation

Previous to the time of *Melloni*, the great difficulty in the experimental study of radiation lay in the fact that there was no instrument sufficiently sensitive to radiation to be of any use in accurate experiments. *Leslie* obtained fairly satisfactory qualitative results with the **differential thermoscope** (page 102), which was used largely in the early days of the study of radiation. The modern form of this instrument, as adapted for the study of radiant heat, comprises two bulbs (Fig. 210) connected by a bent capillary tube and containing ether and ether vapour. The lower bulb is coated with lamp-black, which is the best radiator and absorber of radiant heat (Art. 14 and Art. 16). When radiant heat falls on the lower bulb, its temperature rises and the vapour pressure of the ether is increased; as a consequence, the ether rises in the tube leading to the upper bulb. The greater the quantity of radiant heat falling on the lower bulb the greater the rise of temperature, and consequently the higher the ether rises, and the



FIG. 210.

height can be observed on a scale placed behind the capillary tube. Owing to external changes of temperature the quantitative results obtained with this instrument are not very reliable.

Modern experimenters have used the **thermopile**, which was invented by *Nobili*, and afterwards improved by *Melloni* and others. This instrument consists (see *Hutchinson, Advanced Textbook of Electricity and Magnetism*) of a number of short square rods of bismuth and antimony, arranged alternately side by side, so as to form a bundle having a square cross-section. At the opposite ends of this bundle are the alternate junctions of the bismuth and antimony rods, so that if one end is heated a thermo-electric current is produced. To employ this instrument, it is connected to a galvanometer and one end of the bundle of bismuth-antimony elements is

exposed to the radiation. The absorption of heat by this end produces a current which deflects the galvanometer. Since the thermal effects involved are very small, this deflection may be taken as proportional to the heat absorbed by the exposed end of the thermopile. If this end is covered with a substance which absorbs an equal proportion of all kinds of radiation, then the galvanometer indication is proportional to the intensity of the incident radiation. It will be seen later that lampblack absorbs every kind of radiation to the same degree, and therefore this substance is employed to cover the ends of the thermopile.

As a source of radiant heat may be used a cubical tin can containing boiling water. To increase the radiating power as much as possible, one face of the can is coated with lampblack (Art. 14). This cubical tin can is termed a **Leslie's cube**.

#### 4. Propagation and Transmission of Radiation

The velocities of radiant heat and light in a vacuum are the same, while the velocity of radiation of any particular wavelength through any medium is inversely proportional to the refractive index of the medium for that particular radiation (see Stewart and Satterly, *Textbook of Light*).

An experiment to show that radiant heat and light travel with the same velocity can be performed at the time of a total eclipse of the sun. Direct a thermopile to the position of the sun and wait until it emerges from behind the moon. Observe the galvanometer at the moment the sun shows itself. A deflection occurs immediately, showing that the heat and light take the same time to travel from the sun to the earth.

*Experiment. To show that radiant heat travels in straight lines.*—Take two screens of wood, AB and CD (Fig. 211), and bore a small hole, say 0.5 cm. in diameter, through each. Arrange them parallel to each other, and opposite the hole in AB place a Leslie's cube, H, as the source of heat with the blackened face turned towards AB. The thermopile, T, and its attachments are then placed on the far side of CD, the face of T being towards CD. T is now moved about. In general, no deflection of the galvanometer will be observed.

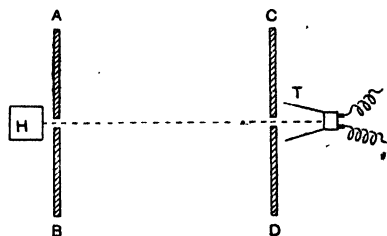


FIG. 211.

If, however, T is placed in the same straight line as the holes in the screens, a large deflection of the galvanometer will be observed.

A body which transmits nearly all the radiant heat which is incident on it is said to be *diathermanous*. A body which absorbs nearly all the incident radiant heat is said to be *adiathermanous*. It follows from a consideration of the energy of the radiation that the passage of radiant heat through a body does not raise its temperature if the body is perfectly *diathermanous*, but does raise its temperature if the body is *adiathermanous*.

### 5. The Law of Inverse Squares

The law which governs the decrease of intensity of radiation

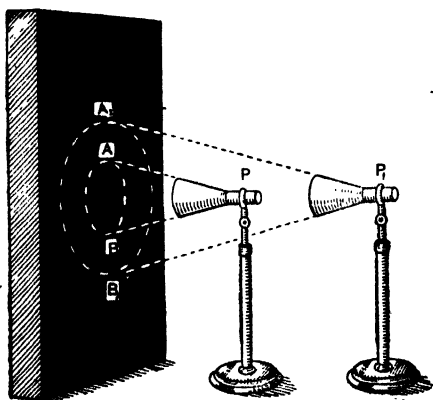


FIG. 212.

with distance is the same as that for light, the two cases being identical (see Stewart and Satterly, *Text-book of Light*). The intensity at different distances from the source of radiation is inversely proportional to the square of the distance.

This may be proved experimentally. A thermopile (Fig. 212) fitted with a reflecting cone is placed in front of a large blackened tin, about 75 cm.  $\times$  75 cm.  $\times$  10 cm., containing boiling water. If the ther-

mopile is kept facing the vessel and moved about along a line perpendicular to the vessel, it is found that, so long as the cone produced by the prolongation of the cone of the thermopile wholly cuts the front face of the vessel, the deflection of the galvanometer remains unaltered.

Consider two positions, P and  $P_1$ , of the thermopile, distant  $x$  and  $y$  respectively from the vessel. It follows by geometry that the areas of the circles, AB and  $A_1B_1$ , from which radiation is received in the two cases are as  $x^2 : y^2$ . Since the galvanometer deflection remains unaltered, the influx of radiation into the thermopile is the same in the two cases, and therefore

$$\frac{\text{The intensity of radiation at P from a small area of the vessel}}{\text{The intensity of radiation at } P_1 \text{ from the same area of the vessel}} = \frac{y^2}{x^2}$$

that is, the intensity of radiation at a point due to a small radiating area is inversely proportional to the square of the distance of the point from the area.

Further, if the surface of the vessel be inclined at any angle to the axis of the thermopile, the galvanometer deflection will not change. This proves that the intensity of the radiation from any surface in any direction is proportional to the cosine of the angle which this direction makes with the normal. For, if the normal to the surface is inclined to the axis of the thermopile at an angle,  $\theta$ , then the area from which the thermopile receives radiation is increased in the ratio,  $\cos \theta : 1$ , and therefore, since the deflection of the galvanometer is unaltered, it follows that the intensity of this radiation decreases in the ratio,  $1 : \cos \theta$ .

By application of these two laws—the law of inverse squares and the cosine law—it can be shown geometrically that, if two bodies, A and B, of equal radiating power are placed near each other, the amount of radiation reaching A from B is equal to that which reaches B from A. Hence, when dealing with the radiation between any two bodies, the radiation received by any one of them may be taken as proportional to that emitted by the other.

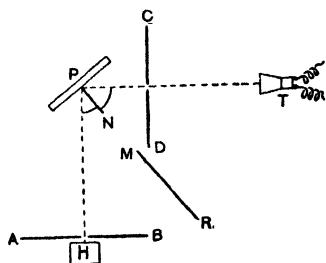


FIG. 213.

## 6. Reflection of Radiant Heat

The laws of reflection for radiant heat are the same as those for light—that is, the angle of incidence is equal to the angle of reflection, and both angles lie in the same plane. This fact is illustrated readily by experiment; indeed, any arrangement intended to exhibit the laws of reflection of light gives exactly similar results with radiant heat.

*Experiment.* To prove that, when radiant heat is reflected at a polished surface, the angle of incidence is equal to the angle of reflection.—As a reflector use a flat polished tin-plate, P (Fig. 213). Place the source of heat, H, a screen, MR, and the plate, P, in position, and move the thermopile, T, about. In some positions there will be deflections of the galvanometer, showing that T is receiving heat. The screen, MR, prevents direct transmission from H to T. Hence, the only conclusion is that heat is reflected at P. To show that the

angle of incidence is equal to the angle of reflection, take the two screens used above (page 335), and place AB in such a position that the incident ray, HP, is inclined at about  $45^\circ$  to the plate, P. Move CD and T about until the galvanometer deflection is a maximum. Join HP and TP, draw the normal, PN, and show that the angles, HPN and TPN are equal.

The following is another common experiment:—Set up two large concave mirrors (Fig. 214), facing each other and about six feet apart, with their axes in the same straight line. Arrange a thermopile so that its lampblackened face lies at the principal focus of one mirror. At the principal focus of the other mirror place an iron sphere heated to red heat. The galvanometer shows a rapid rise of temperature of the thermopile so long as the face is kept at the principal focus of the mirror; but if it is moved into any other position the temperature falls immediately, thus showing that the

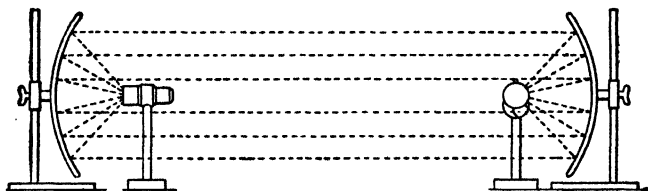


FIG. 214.

radiation from the iron sphere is reflected from one mirror to the other, and then converged to the thermopile. The result is not affected by placing a small screen to prevent the thermopile from being influenced by direct radiation from the iron sphere.

## 7. Reflecting Power

*The reflecting power of a surface is measured by the ratio of the amount of regularly reflected radiation to that of the total incident radiation.* For example, if the radiation incident on a surface be denoted by  $R$ , and the quantity reflected by  $R_r$ , where  $r$  is less than unity, then the reflecting power is measured by the ratio

$$\frac{R_r}{R} = r.$$

This subject was investigated first by *Leslie*, who employed the apparatus shown (Fig. 215).  $H$  represents a Leslie's cube,  $M$  is a concave spherical mirror, so placed relative to  $H$  that the reflected

radiation is brought to a focus at F. The surface whose reflecting power was to be tested was placed at SS' in such a position that it intercepted the radiation converging to F, and reflected it to F', where one of the bulbs of a differential thermoscope, T, is placed. With this arrangement the relative reflecting powers of different surfaces may be determined by noting the indications of T as the surfaces are placed successively at SS'. From his observations, Leslie drew up a table (see Table XXI., page 401) exhibiting the relative reflecting powers of a number of different surfaces for the specific radiation used.

The above method was not very accurate, and moreover does not determine *reflecting power* as defined here. If the thermoscope had been placed first at F, and its indication in that position, before the interposition of a plate at SS', compared with its several indications at F', then the ratio in each case would have given an approximate determination of the *absolute* reflecting power of each surface.

More recent workers have used apparatus similar to that described above (Fig. 213) in which the angle of incidence may be varied. The plate, P, being removed, the thermopile, T, is first placed along HP produced, and the incident radiation from H measured. The plate, P, is then placed in position and the thermopile rotated to catch the reflected rays, the total length of path from H to T being kept the same as before. The results of experiment may be summarised briefly:—

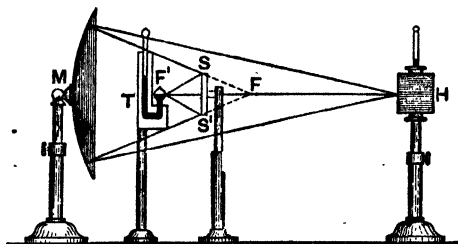


FIG. 215.

- (1) The general laws of reflection of radiant heat are the same as those of light.
- (2) The reflecting power of any surface increases with the degree of polish of that surface.
- (3) The reflecting power of a surface varies with the nature of the source of radiant heat.
- (4) For *diathermanous* substances the reflecting power increases with the angle of incidence, but for metallic surfaces it remains nearly constant for angles of incidence up to about  $70^\circ$ . Above



this limit the reflecting power gradually decreases. *These results are also true for light.*

Polished metals are the best reflectors. Familiar applications of the principles governing the reflection of heat are firemen's helmets, the reflectors of gas and electric fires, etc.

## 8. Diffusion of Radiant Heat

When radiation is incident on a rough or unpolished surface, it is, as it were, broken up by the inequalities of the surface, and undergoes irregular reflection, or *diffusion*. *The diffusive power of a surface is measured by the ratio of the total quantity of diffused radiation to the total quantity of incident radiation.*

Melloni exhibited the existence of diffusion by means of the apparatus described above (Fig. 213). The roughened surface to be experimented on was placed at P, and the thermopile adjusted in the position T. In this and similar positions the thermopile indicated at once the absorption of radiation by the face turned towards P. This radiation could not be *reflected* from the surface at P, for that surface was not polished, and the effect was observed for *all positions* of P in front of the plane of the surface. The effect could be due therefore only to diffusion, or to radiation from the surface, P, heated by direct radiation from H.

Melloni showed that the effect could not be due wholly to this latter cause. For (a) the indication of the thermopile was instantaneous, and reached its maximum at once, whereas, if the radiation from H was first absorbed by the surface and then radiated to T, time would be required for the effect to become appreciable, and the maximum would be attained slowly; (b) the radiation incident on T was of the *same nature* as that coming from H, and different from that which would be radiated by the surface.

The diffusive power of any surface may be determined by the same method as that adopted for the determination of reflecting power. The observations must be taken quickly, however, or there may be complications by the effects of radiation from the surface. The results obtained by recent workers may be summarised:—

(1) The heat diffused in any direction from a given surface varies with the inclination to the surface.

(2) The diffusive power of a surface varies with the nature and material of the surface. In general, a rough, uneven surface, such as that of a fine powder, diffuses best, but this depends on the

*absorbing power* of the material of the surface. For example, a rough lampblack surface would absorb more than 90 per cent. of the incident radiation, and diffuse less than 10 per cent.

(3) The diffusive power of a given surface varies with the source of heat. In general, radiation of low refrangibility tends to be absorbed, while radiation of higher refrangibility tends to be diffused. For example, a white lead surface absorbs about 90 per cent. of the radiation from a source at  $100^{\circ}\text{C.}$ , and diffuses about 10 per cent., but it absorbs only 18 per cent. of solar radiation, and diffuses 82 per cent.

### 9. Refraction of Radiant Heat

The laws of the refraction of radiant heat are identical with those of optical refraction. This can be shown by the following experiment:—

*Experiment.* Arrange the usual apparatus for producing a pure spectrum (see Stewart and Satterly, *Textbook of Light*), using a strip of platinum heated to incandescence by a Bunsen flame, or by an electric current, as the source of light and heat. Adjust the face of a thermopile so as to receive the portion of the spectrum lying beyond the red; the galvanometer at once indicates the absorption of heat. Now rotate the prism so as to displace the spectrum some distance on either side of the thermopile; the galvanometer deflection quickly falls to zero.

Place the thermopile in the same position as before, relative to the visible spectrum; the deflection will increase again to its original value. Now allow the platinum to cool slowly, with the thermopile in position; the deflection shows a slight continuous decrease as the visible spectrum gradually fades out from the violet to the red, but soon after this point is reached a much more marked decrease is observed, indicating that the radiation incident on the thermopile is disappearing in its turn.

The above experiment and others of a similar character show that both the luminous and the non-luminous radiation from an incandescent source of heat are refracted according to the same general laws, and also that the *refrangibility* of the non-luminous portions of the radiation is lower than that of the luminous portion. Prisms and lenses of *rock-salt* should be used in the experiments, because glass absorbs a large percentage of the non-luminous radiation, while rock-salt absorbs less than 10 per cent. of it (see Table XXII., page 401).

### 10. Measurement of Diathermancy

*The proportion of the incident radiation transmitted by a given thickness of a substance is a measure of the power of transmission or diathermancy of that thickness of the substance for the radiation considered, i.e. the transmitting power or diathermancy is measured by the ratio of the transmitted radiation to the total incident radiation. The diathermancy of different substances may be determined by the following experiment:—*

*Experiment.* H (Fig. 216) is the source of heat, S a screen with a circular aperture, *a*, through which radiation from H falls on P, the plate of the substance to be tested. Place the thermopile at T, and note the galvanometer deflection before and after interposing the plate, P. The ratio of these deflections determines the diathermancy of the substance for the thickness considered. Repeat with plates of other substances of the same thickness.

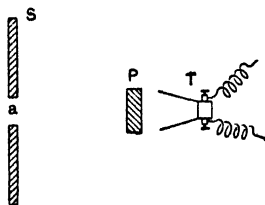


FIG. 216.

Melloni used the method described above to measure the diathermancy of many solids. The results obtained (see Table XXII., page 401) are expressed as the percentages of radiation transmitted by plates 2.5 cm.

thick for the four sources of radiation given at the head of the table. In this table it will be noticed that with all substances except rock-salt the diathermancy increases with the temperature of the source of radiation. This is not always true; it depends on the nature of the rays emitted. Thus glass will transmit a greater proportion of the rays from a piece of incandescent platinum heated in the flame of a spirit lamp than from the flame itself, although the platinum cannot be as hot as the flame.

Melloni also examined the diathermancy of a substance for the radiation transmitted by another substance, and found that a substance is very diathermanous to radiation which has passed already through a plate of the same substance. Thus alum transmitted only 9 per cent. of the radiation from a naked flame, but when the radiation had passed already through an alum plate 0.1 inch thick, 90 per cent. of it was transmitted.

In the case of liquids, Melloni used narrow cells of very thin glass, and observations were taken first with the radiation passing

through the empty cell, and then with the radiation passing through the same cell filled with the liquid to be tested (see Table XXIII., page 401). An Argand burner was used as a source of radiation, and it must be remembered that the rays had to pass through glass both before and after traversing the liquid. The liquid thickness was about 1 cm.

A solution of iodine in carbon bisulphide, though opaque to light, was found to be very diathermanous to radiant heat. Also, it is worthy of note that although alum is considered usually to be adiathermanous, yet the addition of alum to water raises the diathermancy of the latter.

The facts given above are applied sometimes to determine roughly the nature of radiation. For example, if the radiation considered is incapable of transmission by alum, then it must consist entirely of dark heat waves.

*Experiment.* To compare the diathermancies of water and carbon bisulphide. Focus sunlight upon the bulb of an ordinary thermometer, and place between the bulb and the lens a flat glass cell filled with water. Observe the reading of the thermometer, and then replace the cell by a similar one filled with carbon bisulphide. Note that the temperature indicated by the thermometer is higher in the second case, thus showing that carbon bisulphide is more diathermanous than water. If a little iodine is dissolved in the carbon bisulphide, the liquid becomes opaque to light, but is still very diathermanous, thus proving that a substance which is non-transparent to light may be transparent to radiant heat.

Tyndall investigated the diathermancy of gases by enclosing them in a long wide tube fitted with rock-salt ends. A thermopile was placed near one end of the tube, and the source of heat at the other. To render the arrangement more sensitive, a compensating source of heat was employed. This consisted of a cube filled with hot water, and placed in such a position relative to the thermopile as to balance exactly the effect of the radiation from the principal source of heat when the interior of the tube was a vacuum. When different gases were admitted into the tube, the galvanometer was deflected, and the amount of deflection varied with the nature of the gas.

It was found that simple gases were more diathermanous than compound gases, and that the diathermancy of dry air was decreased greatly by the presence of various vapours. For example, water

vapour has a very marked effect, and was found to increase the absorptive power to from 30 to 70 times that of dry air, according to the amount of vapour present. It is now fully established that pure air is highly diathermanous, but that the water vapour and carbon dioxide present in ordinary air possess a well-defined absorbing power.

## II. Influence of Thickness on Transmission (and Absorption)

The influence of thickness on diathermancy was investigated by *Jamin and Masson*. From the results of experiment it was deduced that, when radiation of a definite kind is transmitted through a substance, the amount transmitted decreases in geometrical progression as the thickness increases in arithmetical progression—that is, each layer of the substance, of a given thickness, transmits the same proportion of the radiation which enters it.

Thus, if  $q$  denote the quantity of radiation entering the substance, then the quantity present after traversing unit thickness is  $qa$ , where  $a$  is a constant which is less than unity. Similarly, on transmission through a second layer of unit thickness, the quantity of radiation is reduced to  $qa^2$ ; and therefore, after transmission through  $n$  layers of unit thickness, the quantity of transmitted radiation is given by  $qa^n$ . The constant,  $a$ , has been called the coefficient of transmission.

When radiation of a compound nature is transmitted by any substance, its various constituents are absorbed to different degrees, and thus the nature of the transmitted radiation is subject to continuous change. However, the character of this change is such that the nature of the transmitted radiation tends to become constant and capable of transmission without absorption. For this reason, radiation which has passed through a plate of any substance passes readily with little loss through another plate of the same substance—for example, alum (Art. 10).

**Example.**—A plate of rock-salt 2.5 mm. thick allows 93 per cent. of the incident radiant heat to pass through it. How much will a plate four times as thick transmit? Assume that there is no loss by reflection at the surfaces. Find also the coefficient of transmission of rock-salt.

	93% passes through	2.5 mm. thickness,	
	93% of 93%	" "	5.0 " "
93%	93% of 93%	" "	7.5 " "
93% of 93%	93% of 93%	" "	10 " "

This is equal to abo. 75%, and therefore the coefficient of transmission is 0.75.

## 12. Newton's Law of Cooling

Consider a body placed in an enclosure at a constant temperature slightly lower than that of the body. If the difference of temperature is small enough, it may be assumed that the rate at which the body loses heat is proportional to this difference. Hence, if  $S$  denote the area of the surface of a body,  $t$  the excess of its temperature above that of the enclosure, and  $E$  a constant depending on the nature of its surface and the state of the surrounding medium, then the heat lost in a small interval of time,  $T$ , is given by

$$h = ES t T.$$

Again, if the body be a good conductor of heat, so that its temperature is the same at all points, this loss of heat may be expressed by

$$h = m s \tau,$$

where  $m$  denotes the mass of the body,  $s$  the specific heat of the material, and  $\tau$  the small change of temperature accompanying the loss of heat. Thus:—

$$ES t T = m s \tau;$$

$$\therefore \frac{\tau}{T} = \frac{ES}{ms} t.$$

Thus, the rate of cooling,  $\frac{\tau}{T}$ , is directly proportional to the excess of the temperature,  $t$ , of the body over that of the enclosure. This is Newton's law of cooling.

*Experiment.* To verify Newton's law of cooling.—Place some hot water in a copper calorimeter blackened on the outside, and support it in an enclosure (see Fig. 82). It is essential that the outer double-walled metal vessel be filled with water to maintain a constant temperature. Take readings of temperature and time every  $5^{\circ}$  C. as the water in the calorimeter cools from, say  $80^{\circ}$  C. to about  $35^{\circ}$  C. Plot a graph between temperature and time, and show from it that the rate of cooling is very nearly proportional to the difference of temperature between the water in the calorimeter and the surrounding enclosure.

*Example.*—In a cooling experiment with a mass of water in a blackened copper calorimeter surrounded by air in a larger double-walled copper vessel containing water at a temperature of  $13.7^{\circ}$  C., the times of cooling of the water in the calorimeter through successive  $5^{\circ}$  C. from  $80^{\circ}$  C. to  $75^{\circ}$  C., and so on down to  $55^{\circ}$  C., were 158, 169, 183, 205, 233 sec. Use these observations to verify Newton's law of cooling.

Draw up a table as follows:—

EXCESS TEMPERATURE OF CALORIMETER IN °C.	AVERAGE EXCESS TEMPERATURE, $t^{\circ}\text{C.}$ , DURING GIVEN PERIOD	TIME TO FALL $5^{\circ}\text{C.}$ , IN SECONDS	RATE OF COOLING, $\frac{\tau}{T}$	$t \div \frac{\tau}{T}$
66.3	63.8	158	0.0316	2020
61.3				
56.3				
51.3				
46.3				
41.3				
	58.8	169	0.0295	1990
	53.8	183	0.0273	1970
	48.8	205	0.0244	2000
	43.8	233	0.0215	2040

The approximate constancy of the values in the last column shows Newton's law to be nearly true. Plot a graph between the average excess temperature,  $t$ , against the rate of cooling,  $\frac{\tau}{T}$  (Fig. 217). This graph will be nearly a straight line passing through the origin.

In the case given above, the temperature of the body is higher than that of the enclosure. If the temperature of the body is less than that of the enclosure, a similar relation,

$$\frac{\tau}{T} = \frac{AS}{ms} t,$$

may be deduced in which  $A$  is a constant of like nature to  $E$ .

In the first case the body *emits* heat, the constant,  $E$ , being the coefficient of emission. In the second case the body *absorbs* heat, the constant,  $A$ , being the coefficient of absorption. It will be proved later (Art. 17)

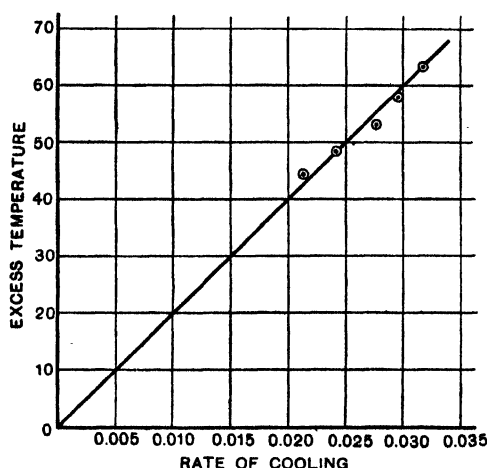


FIG. 217.

that, for a given temperature of the body and a fixed value of  $t$ , the coefficients,  $E$  and  $A$ , have the same numerical value.

### 13. Determination of the Coefficient of Emission

The coefficient of emission of heat has been defined above. *MacFarlane* determined this coefficient by application of the relation  $\tau/T = ES t/ms$ . A copper sphere was allowed to cool in an enclosure maintained at a constant temperature, and the rate of cooling,  $\tau/T$ , was determined. Then,  $S$ ,  $m$ ,  $s$ , and  $t$  being known,  $E$  was calculated readily. It was found that the value obtained was not constant for different values of  $t$ . As  $t$  increased beyond a certain limit, the value of  $E$  also increased, thus showing that Newton's law is approximately correct only within certain comparatively small limits. For example, in one experiment, as  $t$  increased from  $5^{\circ}\text{C.}$  to  $60^{\circ}\text{C.}$ ,  $E$  increased by about 25 per cent.

**Example.**—In the example quoted above (Art. 12), the mass of water together with the water equivalent of the calorimeter was 63 grm., and the surface area of the calorimeter, which was almost full of water, was about 100 sq. cm. Find an approximate value of the coefficient of emission.

From above,

$$\begin{aligned} E &= \frac{ms}{S} \cdot \frac{\tau}{T} \cdot t, \\ &= \frac{63 \times 1}{100} \div 2020, \\ &= 3 \times 10^{-4} \text{ calorie per sq. cm. per sec. per} \end{aligned}$$

degree C. excess temperature.

### 14. Comparison of Emissive Powers

The determination of the *comparative emissive powers* of different surfaces is a simpler matter than determining the *coefficient of emission* for a given substance.

*Leslie*, and later *Melloni*, made comparative determinations for a large number of substances, both using almost the same method. *Leslie* employed as source of heat a thin metal cube containing boiling water. The sides of this cube were covered with the substances whose emissive powers were to be compared. The radiation from one face of the cube was concentrated by a concave mirror on to one of the bulbs of a differential thermoscope. The indication being noted, the other faces of the cube were tested in the same way, and the relative emissive powers were taken as proportional to the corresponding indications of the thermoscope. *Melloni*, adopting the same method, employed a thermopile instead of the differential thermoscope.

**Experiment.** Take a cubical tin can, cover one vertical face with lampblack, another with white lead, a third with paper, and polish the fourth. Fill the can with water and keep it boiling with



a protected flame. Bring the face of a thermopile, or the blackened bulb of an air thermoscope, to the same distance, say one inch, from each side in turn, and for the same time, say three minutes. Note that the indication of the thermopile, or the thermoscope, is greatest when opposite the lampblack and least when opposite the polished surface. Other surfaces may be compared in the same way.

The arrangement of apparatus adopted by more recent workers is indicated (Fig. 218).  $H$  is a Leslie's cube,  $S_1$  is a screen covered with lampblack on the side next  $H$ , and polished on the other side. This prevents heat being reflected from the front surface back to  $H$ , and thence to the thermopile,  $T$ , and also diminishes radiation from the other surface towards  $T$ .  $S_2$  is another screen to shield  $T$  from any radiation from  $S_1$ .

It was found that the radiation emitted from polished metallic surfaces was too small to be compared accurately directly with that

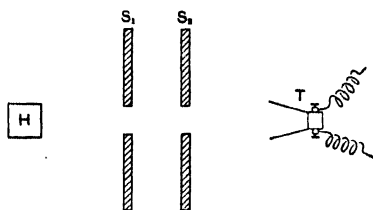


FIG. 218.

from a lampblack surface. To remedy this defect, a diaphragm pierced with two holes of different sizes may be employed, so that by using the smaller hole with the lamp-black surface, and the larger with the metallic surface, comparable indications can be obtained. Of course, the ratio

of the amounts of radiation passing through the holes when used separately with the same source of radiation must be determined first, and then the necessary correction for the difference in size of the holes applied to the results of the first experiment.

Some of the results obtained are shown (Table XXIV., page 401).

**Experiment.** Obtain the cooling curves for water in a tin can, whose outside surface is (i) polished, (ii) jacketed with cotton-wool, (iii) coated with lampblack; also (iv) when the blackened can is suspended within a larger one whose inside surface is bright, and (v) as in (iv), but when the inside surface of the larger can is blackened. Use the same quantity of water in each experiment, begin observations when its temperature is about  $80^{\circ}\text{C}$ ., and continue to about  $40^{\circ}\text{C}$ . Tabulate the observations in each case and plot all to a large scale on one sheet of graph paper. The curves obtained will show roughly the *emissive* powers of the

surfaces when (i) polished, (ii) lagged—that is, jacketed with a poor conductor, (iii) blackened, (iv) when screened by a reflecting surface, (v) when screened by a blackened surface.

### 15. Stefan's Law

It has been shown by experiment that the emissive power of a surface varies greatly with the temperature. Several more or less complicated relationships have been deduced from the results of experiments to express the law of cooling in terms of the temperature conditions.

*Dulong and Petit* made a laborious investigation of this subject. It was found that for a given excess of temperature the rate of cooling of a body depended not only on the temperature of the body, but also on that of the enclosure. The relation established in this connexion may be expressed as follows:—*For a given excess of temperature the rate of cooling increases in geometrical progression as the temperature of the enclosure increases in arithmetical progression.*

Later *Stefan* corrected the results of *Dulong and Petit's* experiments, and found that they might be expressed by a very different relation. It was shown that the emissive power of a body cooling under given conditions is proportional to the fourth power of its absolute temperature, and that this law agrees more closely with the results of experiment than does that deduced by *Dulong and Petit*.

When a cooling body is surrounded by a gas, its rate of cooling is much more rapid than *in vacuo*, and is found to depend on the pressure of the gas. In *MacFarlane's* experiment (Art. 13), it was calculated that, when the copper sphere and enclosure were covered with lampblack, and cooling took place in air at the normal pressure, one half of the cooling effect was due to air convection.

### 16. Absorption of Heat

The coefficient of absorption has been defined above (Art. 12) in connexion with the coefficient of emission. The relation between these two coefficients seems to indicate that the absorbing power of any surface is proportional to its emissive power for the same kind of radiation. Experiment has shown that this is so.

*The "absorbing power" of any surface is defined as the proportion of the incident radiation which it absorbs, i.e. it is measured by the ratio of the radiation absorbed to the total incident radiation. The absolute determination of absorbing power, as thus defined, is*

somewhat difficult; but in some cases it may be deduced indirectly from the results of other experiments (Art. 2).

The comparison of the absorbing powers of different substances is effected more easily. *Melloni* employed for this purpose the arrangement of apparatus indicated (Fig. 219). *H* represents the source of heat, *S* a perforated screen, *T* a thermopile, and *C* a sheet of very thin copper plate coated on the front surface with the substance to be tested, and on the surface facing the thermopile with lampblack. The first substance tested was lampblack, which, as in the case of emission (Art. 14), was taken as the standard substance. The relative absorbing powers of different substances were then deduced from the data of the experiments as follows:—

Let  $Q$  denote the radiation incident on the first surface of *C*, when covered with the substance to be tested. Then, if  $\alpha$  denote the absorbing power of this substance, the quantity of heat absorbed is given by  $Q\alpha$ . This absorbed heat raises the temperature of the copper until the loss by radiation from its surfaces is equal to the gain of heat. Hence, if  $t$  denote the rise of temperature,  $E$  the coefficient of emission of the front

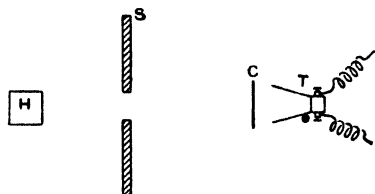


FIG. 219.

surface, and  $E'$  the coefficient of emission of the surface facing the thermopile, then:—

$$Q\alpha = S(E + E')t,$$

where  $S$  denotes the area of the surfaces. Similarly, if both surfaces of the plate be covered with lampblack, then:—

$$Q\alpha' = 2SE't',$$

where  $\alpha'$  denotes the absorbing power of lampblack. Hence:—

$$\frac{\alpha}{\alpha'} = \frac{E + E'}{2E'} \cdot \frac{t}{t'}.$$

But the galvanometer deflections,  $d$  and  $d'$ , are proportional to the heat radiated from the adjacent surface of the plate, hence

$$\begin{aligned} \frac{d}{d'} &= \frac{SE't}{SE't'} = \frac{t}{t'}; \\ \therefore \frac{\alpha}{\alpha'} &= \frac{E + E'}{2E'} \cdot \frac{d}{d'}. \end{aligned}$$

The results obtained by Melloni are shown in Table XXV., page 401. It will be seen that some of these results are identical with those obtained for relative emissive powers (Art. 14) at  $100^{\circ}\text{C}$ .

The same apparatus served to determine the variation of the absorbing power with the nature of the source of heat. In general, the absorbing power is greater the lower the temperature of the source. Hence, when radiation of a complex nature is incident upon any surface, some of the constituents are absorbed, the remainder being reflected or diffused according to the conditions which obtain. This *selective absorption* gives rise to the phenomenon of *thermochrose*, which corresponds to *colour* in the case of light. Every surface has the power of absorbing radiation of a fixed nature made up of constituents of definite refrangibility, or wave-length. Hence, when compound radiation containing all or any of these constituents is incident on the surface, these are absorbed, and the character of the unabsorbed radiation is changed thereby, giving rise to *thermochrose* or *colour*, according to the wave-length of the radiation concerned (see Stewart and Satterly, *Textbook of Light*).

It should be noticed that absorption differs from the other phenomena considered in this chapter in that, after absorption, the radiation ceases to exist as radiation, and becomes ordinary heat due to molecular motion. Hence, when a body *absorbs* radiation it rises in temperature, whereas a body which transmits radiation does not rise in temperature.

When an adiathermanous substance absorbs heat, it is probable that the absorption takes place at the surface, or in a very thin superficial layer; but in a diathermanous substance absorption takes place during transmission (Art. 10), and probably at the surface also. Lampblack is the only one of the substances which have been tested which does not exhibit selective absorption. It absorbs all kinds of radiation to the same degree.

The following experiments may be carried out to show that a blackened surface absorbs radiant heat to a greater extent than a polished surface:—

*Experiments.* (a) Take two exactly similar polished tins, such as cigarette tins; blacken the outer surface of one of them by means of an oil-lamp burner. Fill both with water, and set them in front of a bright fire. After half an hour test the temperature of the water in each with a thermometer. • The water in the blackened tin will be the hotter.

(b) Fit up the apparatus illustrated (Fig. 220). A is a sheet of thin copper with a brightly polished surface facing B, another similar sheet, having a lampblackened surface turned towards A. A and B are connected by a copper wire, *cc*. Two iron wires, *i* and *i'*, are joined, as shown, to the outer surfaces of A and B, and to the galvanometer, G. A copper-iron thermo-electric circuit (page 30) is thus formed, having the junctions at A and B. A heated metal sphere, M, is supported midway between A and B, so that the copper plates are exposed equally to its radiation. In a short time the galvanometer shows a gradually increasing deflection, indicating that the junction at B is being heated more rapidly than that at A.

### 17. Theoretical Relations Between Reflection, Diffusion, Absorption, and Emission

Let  $Q$  denote the quantity of radiation incident on the surface of a body. This, in the most general case, may be divided into two parts;  $Q'$ , which is arrested at the surface, and  $q$ , which is transmitted by the substance of the body. That is,  $Q = Q' + q$ . Now:—

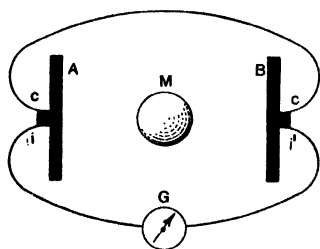


FIG. 220.

$Q' = Q(r + d + a)$ , where  $r$ ,  $d$ , and  $a$  are the portions of  $Q$  which are reflected, diffused, and absorbed. The quantity,  $q$ , is diminished by continuous absorption during transmission, and, if  $a$

denote the coefficient of transmission (Art. 11), then  $qa^n$  gives the intensity of the transmitted radiation after passing through a thickness,  $n$  cm., of the substance.

Some particular cases of this general case will now be considered. In each case the substance is assumed to be *adiathermanous*, so that  $q$  is zero, and therefore  $Q' = Q$ .

(I) SURFACE POLISHED.—If the polish is sufficiently perfect,  $d$  is zero. Hence:—

$$Q = Q(r + a); \therefore 1 = r + a,$$

$$\text{i.e. } a = 1 - r.$$

Thus, the absorbing power of the surface is complementary to its reflecting power. Hence, when a reflecting surface of this nature reflects well, it absorbs badly—that is, when  $r$  is large,  $a$  is small.

(2) SURFACE ROUGH.—The surface being unpolished,  $r$  is zero. Hence:—

$$Q = Q(d + a);$$

$$\therefore a = 1 - d.$$

That is, the absorbing power of the surface is complementary to its diffusive power. Hence, when a surface diffuses well, it absorbs badly.

From these two cases it is evident that, under the conditions considered,  $a$  can be calculated when  $r$  or  $d$  is known.

(3) SURFACE IMPERFECTLY POLISHED.—In this case we have the following relation:—

$$Q = Q(r + d + a);$$

$$\therefore a = 1 - r - d = 1 - (r + d).$$

That is, the absorbing power of the surface is complementary to the sum of the reflecting and diffusive powers. By polishing the surface,  $r$  is increased and  $d$  is decreased, so that the sum,  $r + d$ , may remain constant, increase or diminish. That is, the absorbing power of a surface may remain constant for different degrees of polish, or may increase or diminish with the degree of polish.

Since the values of  $r$  and  $d$  vary with the angle of incidence of the radiation, it follows that the absorbing power,  $a$ , also varies with the angle of incidence in such a way as to be always complementary to  $r$ ,  $d$ , or  $(r + d)$ .

If the diathermancy of a plate of rocksalt be tested *for radiation* from a hot piece of the same substance, it will be found to be very small; a thin plate absorbs more than 75 per cent. of the radiation; and, if the plate be at the same temperature as the radiating piece, it will be found that none of the incident radiation is transmitted by it. Hence, the radiation absorbed by any substance at a given temperature is of the same nature as that emitted by the substance at the same temperature. This may be compared with the production of the Fraunhofer lines in the solar spectrum (see Stewart and Satterly, *Textbook of Light*). From this it follows that the absorbing power of any substance is proportional to its emissive or radiating power at the same temperature.

The colour of a body also has some influence on its absorbing power. For example, a white coat absorbs less heat in the sunshine than a black one, and hence white or light-coloured clothing is worn in very hot countries.

### 18. Prevost's Theory of Exchanges

This theory asserts that *every body emits radiation in all directions to an extent determined only by its temperature and the nature of its surface, and that it absorbs radiation from all sources to which it is exposed.*

Suppose that in the experiment on reflection (page 338), a piece of ice takes the place of the hot iron sphere (Fig. 214). It will be found that the thermopile indicates a fall of temperature. This result is explained very neatly by the above theory. The ice radiates in all directions at a rate dependent on its temperature. A portion of this radiation is reflected from one mirror to the other, and thence to the thermopile. Similarly, the thermopile radiates in all directions at a rate dependent on its temperature, and a portion of this radiation, after reflection by the mirrors, is concentrated on the ice. Hence, considering the thermopile, it gains heat by radiation from the ice, and loses heat by its own radiation; and in this case, since the temperature of the thermopile is higher than that of the ice, the loss is greater than the gain, and the temperature falls. In the experiment with the hot iron, the gain is greater than the loss, and the temperature of the thermopile rises.

When bodies are at the same temperature, each loses as much heat by its own radiation as it gains by radiation from surrounding bodies, and thus the temperature of each remains constant. Consider an enclosure maintained at a constant temperature, and having a thermometer suspended in its interior. Whatever may have been the initial temperature of the thermometer, ultimately it takes and retains the constant temperature of the enclosure. When this is the case, the heat which the thermometer gains from the walls of the enclosure equals that which it loses by its own radiation. That is, the radiation absorbed by any body at a given temperature is equal to and identical with the radiation emitted by the same body at the same temperature. This result has been deduced already from experiment, and therefore it affords an indirect, experimental proof of the theory of exchanges.

Again, if a large number of thermometers, whose surfaces are covered with different substances, are suspended in the enclosure, ultimately all take up a common constant temperature equal to that of the enclosure. Now, considering any one of these thermometers, there is evidently a more complex system to deal with than in the case just considered. The thermometer receives radiation from the walls of the enclosure, and also from each of the

other thermometers. The radiation from the walls of the enclosure is of a definite kind, determined by the nature of the surface. Also, the radiation from each of the thermometers is of a definite kind, similarly determined; but the nature of the surface being different in each case the radiation emitted is also different. Hence, the thermometer considered receives a large number of different kinds of radiation, and emits one kind of radiation determined by the nature of its own surface. Since the temperature remains constant, however, it follows that the heat gained must equal the heat lost—that is, the radiation emitted must be identical in quantity and *quality* with that absorbed.

This statement seems to imply that the radiation emitted by any body is determined by the radiation it absorbs, and not by any inherent property. This is not the case, of course; the radiation emitted by any body cannot be controlled by any merely external circumstance. If the thermometer emits radiation other than that which it absorbs—that is, *other than that which is emitted by the bodies from which it receives radiation*—then this radiation, since it is not emitted by the other bodies, cannot be absorbed by them, and therefore is returned to the thermometer by reflection or diffusion, and is there absorbed. Thus, it is evident that in an enclosure of this nature the stream of radiant heat is constant in quantity and quality, for each surface restores by its own radiation a quantity exactly equal and similar to that which it absorbs.

For example, suppose four of the thermometers to have surfaces of lampblack, gold-leaf, glass, and powdered silver, respectively. The lampblack surface absorbs nearly all the incident radiation, and emits a corresponding quantity. The gold-leaf surface reflects a large percentage and absorbs the remainder; hence, it emits a small quantity only. The glass surface reflects and transmits a proportion depending on the nature of the radiation, and absorbs the rest, which corresponds to the radiation it emits. The powdered silver surface diffuses a large amount, and therefore absorbs and emits but little. The thermometers appear alike in temperature.

From what has been said above, it will be seen that for any two bodies, A and B, exposed to each other's radiation at the same temperature, there is a *constant, interchangeable* quantity of radiation, capable of absorption by each. Thus, of the radiation emitted by A, a portion,  $q$ , of fixed quantity and quality, is absorbed by B; this is again emitted by B, forming a portion of the total radiation emitted by that body. When this radiation from B falls upon A,



the portion,  $q$ , only is absorbed, for every constituent capable of emission by B and absorption by A is capable also of emission by A and absorption by B, and therefore is included in the quantity,  $q$ . Hence, if  $mq$  denotes the radiation emitted by A, and  $nq$  that emitted by B, then

$$\frac{\text{Radiating power of A}}{\text{Radiating power of B}} = \frac{m}{n}.$$

$$\frac{\text{Absorbing power of A for radiation emitted by B}}{\text{Absorbing power of B for radiation emitted by A}} = \frac{q/nq}{q/mq} = \frac{m}{n}.$$

That is, the absorbing power of any substance, A, for radiation emitted by any other substance, B, at the same temperature, is to the absorbing power of B, for radiation emitted by A, as the radiating power of A is to that of B.

For example, consider the case of a thermometer suspended in an enclosure at constant temperature. Suppose the radiating power of the walls of the enclosure to be five times that of the thermometer, and that the walls absorb one-fourth of the radiation from the thermometer. Then, in order that the temperature of the thermometer may remain constant, it must absorb a quantity of heat equal to one-fourth of its own radiation—that is, one-twentieth of the radiation from the walls of the enclosure which, by hypothesis, is five times that from the thermometer. Hence, the radiating and absorbing powers of the thermometer and the walls of the enclosure have the common ratio, 1 : 5. This relation is true for each constituent of the radiation to which it applies.

### 19. Radiation of Gases

In general, gases radiate badly, but in most cases the phenomena of selective absorption and radiation are very strongly marked.

The radiation from a solid, at a given temperature, is included generally within a certain range of wave-length. As the temperature rises, this range is extended in the direction of increasing refrangibility, while each constituent increases in intensity. On the other hand, gases emit radiation made up of one or more constituents of definite wave-length. As the temperature rises, other constituents of shorter wave-length may be added, and the intensity of each of the original constituents is increased.

In the construction of furnaces, the hot gases are made to play on some substances, such as fire-brick, which are good radiators. These become heated by direct contact with the hot gases and then radiate freely in all directions. Asbestos radiants used in gas-fires

and fire-clay bricks used in ordinary grates further illustrate this principle.

The oxides of the rare elements, thorium and cerium, emit light very readily when hot, hence their use in the **Welsbach** gas mantle.

## 20. Illustrative Experiments and Phenomena

Some natural phenomena and a few more simple experiments which illustrate the principles and laws deduced in this chapter will be considered here.

The effect of the nature of the surface of a body on radiation may be seen by noting the rate of cooling of water in a vessel whose surface can be varied. If the vessel has a brightly polished metallic surface the water cools very slowly, but if covered with lampblack the rate of cooling is very much faster (Art. 14). For this reason vessels, such as teapots, intended to keep their contents hot, should have brightly polished surfaces. Similarly, if a vessel having a brightly polished surface is exposed to radiation, it absorbs heat very slowly, whereas, if the surface is rough and blackened, the incident radiation is absorbed more rapidly. The exterior of a calorimeter is kept polished so that it may neither radiate nor absorb heat. Hot-water pipes and radiators are blackened to increase the radiation from them.

These illustrations show that a good reflecting surface radiates badly and also absorbs badly. Lampblack is the best radiator and absorber of heat known, but it is also the worst reflector. Experiments which illustrate these results have been described above, and others will be described here.

*Tyndall* devised the following:—Write a word with ordinary ink on a piece of thin bright platinum foil, and then heat the foil to a bright white heat. It will be seen that the written characters, which have a rough surface of iron oxide, glow much more brightly than the rest of the foil. If the reverse side of the foil, on which there is no writing, is observed it will be seen that the writing is visible on it as a dark pattern on a bright ground. The letters, on account of the nature of their surface, radiate more than the foil, and therefore cool more rapidly. Hence, the foil immediately underlying the writing also cools by conduction more rapidly than the rest of the foil, and thus appears dark in comparison with the other portions of the same surface.

Obtain a piece of white earthenware bearing a dark-coloured design. When cold, the design absorbs most of the light falling on

it; the rest of the earthenware appears white by diffusion. Now heat the earthenware in a fire or gas furnace. When quite hot, withdraw it and place it in the dark. It will be seen that the design now gives off more light than the other portions of the earthenware.

*Ritchie* devised a very convenient form of apparatus to show the equality of the radiating and absorbing powers of a surface. It comprises (Fig. 221) two cylindrical reservoirs containing air, joined together by a glass tube bent twice at right angles and supported on a stand behind the two upright glass tubes. This arrangement constitutes a Leslie differential thermoscope.

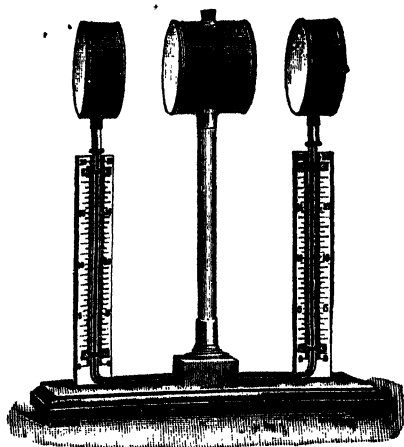


FIG. 221.

Between the two reservoirs is a third and larger one which can be filled with hot water and which is movable along a horizontal support. Each small reservoir has one face coated with lampblack, the other being polished bright. The black face of one and the bright face of the other are towards the centre reservoir. The centre reservoir similarly has one face black and the other polished, and it is placed so that its bright face is towards the black face of one small reservoir and its black face towards the bright face of the other small reservoir.

When the centre reservoir is filled with hot water its bright face radiates to the black face of a small reservoir, and its black face to a bright face. It is found that, when the centre reservoir is midway between the other two, the liquid in the tube of the thermoscope does not move, indicating that the air in the two small reservoirs is at the same temperature.

The various phenomena of diathermancy also are capable of simple illustration. For example, if radiation is transmitted through a plate of ice, the interior of the plate begins to melt, showing beautiful hexagonal ice crystals; but the radiation, after passing through this plate, may be passed through another plate of

ice without causing the least melting. This shows that the absorption which radiation undergoes during transmission through any substance is such as to fit it for further transmission without absorption.

Again, the glass fire-screens used occasionally are applications of the fact that the diathermancy of glass varies with the nature of the radiation. The radiation from the fire falling on the screen is partly absorbed and partly transmitted; the more refrangible luminous portion is transmitted, while the less refrangible portion, of greater heating power, is absorbed and afterwards radiated by the screen. In this way the cheerful firelight is transmitted, but the most intense heat rays are absorbed, and afterwards emitted by the screen as radiation of a less intense nature.

The use of glass in *hot-houses* may be explained. Of the solar radiation incident on the glass only the more refrangible luminous portion is transmitted. This portion, however, forms a large percentage of solar radiation, and has considerable heating effect; hence, when absorbed by the objects within the hot-house, it gradually raises their temperature. The radiation from these objects, being of low refrangibility, is not transmitted by the glass, and cannot escape in this way to the exterior. This radiation, however, is absorbed by the glass; but, owing to the absorption of a portion of the solar radiation, the glass is at a higher temperature than the objects inside the hot-house, and therefore returns to them by its own radiation more than it receives. In this way the temperature of the interior rises gradually, and will continue to do so until it attains the temperature of the glass.

The water vapour in the atmosphere acts in much the same way towards the earth as the glass does towards the objects in a hot-house. Dry air is very diathermanous to radiant heat, but the absorptive power of air charged with water vapour is from 30 to 70 times as great as that of dry air (see Art. 10), while it is still very transparent to rays of light. Thus the earth is protected by the absorptive action of the water vapour in the atmosphere from the more intense heat rays of the sun; but, when the warmed earth begins to radiate its heat in rays of low refrangibility, these rays find a most effectual barrier to their escape in the water vapour, which absorbs them freely and becomes warmed thereby. In this way extremes of temperature are avoided—the direct heating effect of the sun during the day and the loss of heat by radiation during the night are both diminished. In summer the plains and valleys

especially are covered by a protecting stratum of vapour which serves to prevent the escape of radiant heat, and when night falls they remain comparatively warm. But sandy deserts, mountain tops, and elevated table-lands, above which there is much less vapour, cool down quickly.

In districts where little water vapour is present in the atmosphere—for example, in the Sahara desert—the days are intensely hot and the nights extremely cold. Probably other causes have something to do with these and similar results, but the action of water vapour undoubtedly has an important bearing on the question.

## CHAPTER XVIII

### KINETIC THEORY OF GASES

REFERENCE has been made (page 3) to the fact that any body consists of *molecules* which are supposed to be vibrating to and fro, at a rate dependent on the temperature. From very early times, the phenomena of the compressibility of matter in its three possible states—solid, liquid, and gas—the solution of solids in liquids, the diffusion of fluids, the expansion of gases, etc., have led to the idea of matter being constituted of particles or *molecules*, separated from each other by minute distances which differ in the different states of matter.

#### 1. Molecular Structure of Matter

A *molecule* is defined as *the smallest portion of a substance which can exist in a free state and retain the properties of that substance.*

The distinguishing property of a solid is that it can retain its shape for an apparently indefinite period. From this it is assumed that the molecules cannot move about from one part of the substance to another. Also, solids possess cohesion, and a great deal of work is required to remove one portion of a solid from another. This suggests that there is considerable force exerted between the molecules. Again, expansion on heating, conduction of heat, and the radiation of heat, indicate some movement of the molecules. Each molecule is regarded as capable of vibrating about a mean position, but not of permanent displacement.

In the case of liquids, such phenomena as diffusion show that the molecules can move about freely from one part to another. At the same time, a liquid has a definite volume at any chosen temperature, and under suitable conditions may possess great cohesion, so that the molecules must be regarded as under the influence of each other's force.

In the case of gases, the phenomenon of diffusion clearly demonstrates the existence of molecular motions. A gas has the property of indefinite expansion and almost negligible cohesion. The molecules may be regarded, therefore, as moving about freely

and not to any great extent under the influence of each other's action. There are many simple illustrations of the phenomenon of diffusion in gases. For example, if a small quantity of a gas such as ammonia is introduced into a room, its presence in every part of the room is evident in a very short time. Again, if two spherical vessels are connected one above the other, the upper one containing hydrogen and the lower containing a dense gas such as carbon dioxide, and a tap connecting them is opened, then it is found that, after a comparatively short time, *both* vessels contain *both* gases in exactly similar proportions. Lastly, the great extent to which the volume of a gas can be reduced by pressure suggests that the molecules occupy only a very small fraction of the whole volume of the gas.

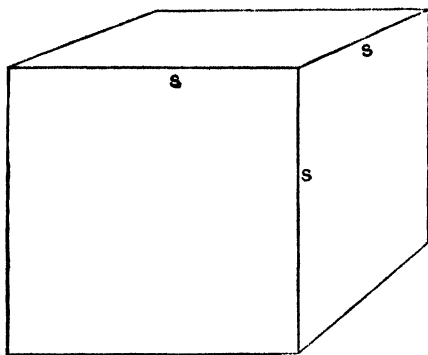


FIG. 222.

## 2. The Pressure of a Gas

The kinetic theory of gases was established chiefly by Clausius and Maxwell. The basis of the theory is that an ideal gas is regarded as made up of a very large number of particles, or molecules, of negligible size compared with the volume of the gas, moving about in all directions with great velocity, constantly

colliding with one another and constantly bombarding the walls of the enclosure containing the gas. No loss of energy occurs at these collisions, each molecule rebounding from the walls with the same velocity as that with which it strikes them. The *pressure* exerted by the gas is regarded as due to this bombardment by the molecules. Any mutual force of attraction between the molecules is assumed to be negligible.

Suppose the gas is contained in a cubical enclosure (Fig. 222), the length of the side of the cube being  $s$ . Let the total number of molecules be  $N$ , and the mass of each molecule be  $m$ . When a molecule of mass,  $m$ , travelling with velocity,  $u$ , perpendicularly to the walls of the containing vessel, meets the wall, it is first stopped and loses *momentum*,  $mu$ . Then, it rebounds from the wall with

velocity,  $u$ , and acquires momentum,  $-mu$ . The total change of momentum is thus  $2mu$ , and if  $n$  such impacts take place per second on each unit area of the wall, the total momentum given to the molecules per second is  $2nm u$ ; that is, there is a rate of change of momentum of  $2nm u$ . But the rate of change of momentum is equal to the force exerted on the wall, and therefore it follows that this is the pressure on the wall due to the bombardment of the molecules.

Now, if there are  $N$  molecules in unit volume of the gas, the molecules moving indiscriminately in all directions, their velocities may be resolved parallel to the three rectangular axes,  $x$ ,  $y$ , and  $z$ , parallel to three adjacent edges of the cube. Since these directions are mutually at right angles, by the resolution of velocities, the resultant velocity,  $\bar{u}$ , is given by the relation,

$$x^2 + y^2 + z^2 = \bar{u}^2.$$

Each of the components can be dealt with separately. Considering the pair of walls of the cube *perpendicular* to the  $x$  axis, a molecule starting at one wall will travel to the other wall, rebound, and reach the wall from which it started in the time it takes to travel a distance,  $2s$ , with velocity,  $x$ ; that is,  $\frac{2s}{x}$  sec. Therefore,

it will collide with this face  $\frac{x}{2s}$  times per sec. Hence, the rate of change of momentum is  $\frac{x}{2s} \times 2mx = \frac{mx^2}{s}$ , which is the force exerted by this molecule.

Similarly, on each of the walls perpendicular to the  $y$  axis, there is a force  $\frac{my^2}{s}$ , and to the  $z$  axis,  $\frac{mz^2}{s}$ . The total force exerted on all the faces is thus

$$\frac{2mx^2}{s} + \frac{2my^2}{s} + \frac{2mz^2}{s} = \frac{2m\bar{u}^2}{s}.$$

If another molecule had a velocity  $\bar{u}_1$ , the total force exerted by it on all the walls would be  $\frac{2m\bar{u}_1^2}{s}$ . Thus the total force exerted by all the  $N$  molecules would be given by:—

$$\text{Total force} = \frac{2m}{s} (\bar{u}^2 + \bar{u}_1^2 + \bar{u}_2^2 + \dots),$$

where  $\bar{u}$ ,  $\bar{u}_1$ ,  $\bar{u}_2$ , etc., are the respective velocities of the  $N$  molecules.



If the mean value of  $(\bar{u}^2 + \bar{u}_1^2 + \bar{u}_2^2 + \dots)$  is denoted by  $\bar{U}^2$ , then the total force is given by:—

$$\text{Total force} = \frac{2mN\bar{U}^2}{s}.$$

The quantity,  $\sqrt{\bar{U}^2}$ , is known as the **root mean square velocity** of the molecules.

The total area of the surface of the cube is  $6s^2$ , and the above total force,  $\frac{2mN\bar{U}^2}{s}$ , is distributed over this area, Hence the *force per unit area*; that is, the pressure,  $P$ , is given by:—

$$P = \frac{2mN\bar{U}^2}{s} \div 6s^2 = \frac{1}{3} \cdot \frac{mN\bar{U}^2}{s^3}.$$

But  $s^3 = V$ , the volume of the cubical enclosure;

$$\therefore P = \frac{1}{3} \frac{mN\bar{U}^2}{V}.$$

Using this relation, it will now be shown how the various gas laws follow from the kinetic theory of gases.

### Temperature

The kinetic energy of a molecule of the gas is given by  $\frac{1}{2}m\bar{u}^2$ , and the total kinetic energy is  $\frac{1}{2}mN\bar{U}^2$ . If energy is supplied to the gas and its temperature is raised, the increase in energy must be represented by increased kinetic energy of the molecules. This means that the quantity  $\sqrt{\bar{U}^2}$  must increase. On this theory, therefore, an increase of temperature means an increase in the value of  $\sqrt{\bar{U}^2}$ . Also, if  $\sqrt{\bar{U}^2} = 0$ , that is, if the molecules are stationary, the temperature must have reached the lowest possible limit, or the **Absolute zero**.

### 4. Boyle's Law

The above relation (Art. 2) may be written:—

$$PV = \frac{1}{3}mN\bar{U}^2.$$

But  $mN$  is the total mass of the gas,  $M$ ;

$$\therefore PV = \frac{1}{3}M\bar{U}^2.$$

If the temperature remains constant,  $\sqrt{\bar{U}^2}$  remains constant. Thus, for any given mass of gas at constant temperature,

$$PV = \text{a constant.}$$

This is a statement of *Boyle's law*, and it is seen that the law follows at once from the kinetic theory.

### 5. Charles's Law

If it is assumed that the addition of equal amounts of energy produces equal increments of temperature, that is, that the thermal capacity of the gas remains constant at all temperatures, then the internal energy of a given mass of gas will be proportional to its absolute temperature. Thus

$$\frac{1}{2}mN\bar{U}^2 \propto T.$$

$$\text{But, } PV = \frac{1}{3}mN\bar{U}^2; \therefore PV \propto T,$$

$$\text{or } PV = RT, \text{ where } R \text{ is a constant.}$$

This is the characteristic equation of a perfect gas (page 102).

### 6. Graham's Law of Diffusion

*Graham* found that the rate of diffusion of a gas varies inversely as the square root of the density of the gas.

$$\text{Now } P = \frac{1}{3} \cdot \frac{mN\bar{U}^2}{V} = \frac{1}{3} \cdot \frac{M\bar{U}^2}{V} \quad (\text{where } M = \text{total mass of gas}).$$

$$\text{But } \frac{M}{V} = \rho, \text{ the density of the gas; } \therefore P = \frac{1}{3}\rho\bar{U}^2.$$

This means that for any particular pressure the value of  $\rho\bar{U}^2$  is the same for all gases, or that

$$\bar{U}^2 \propto \frac{1}{\rho},$$

which conforms with *Graham's law*. The relation,  $P = \frac{1}{3}\rho\bar{U}^2$ , may be used to calculate the value of the *root mean square velocity* of the molecules of a gas.

**Example.**—The density of hydrogen at 0° C. and 760 mm. pressure is 0.0000896 gm. per c.c. Find the root mean square velocity of the molecules of the gas.

$$\text{Here } P = 76 \times 981 \times 13.59 \text{ dynes per sq. cm.}$$

$$\text{Hence, } \bar{U}^2 = \frac{3 \times 76 \times 981 \times 13.59}{0.0000896}$$

$$\text{and, } \sqrt{\bar{U}^2} = \sqrt{\frac{3 \times 76 \times 981 \times 13.59}{0.0000896}} = 184000 \text{ cm. per sec.}$$

### 7. Avogadro's Hypothesis

Suppose there are two gases, each at the same pressure,  $P$ . Let  $N_1$  be the number of molecules per unit volume,  $m_1$  the mass of each molecule, and  $\sqrt{\bar{U}_1^2}$  the root mean square velocity of the molecules of one gas, and let  $N_2$ ,  $m_2$ , and  $\sqrt{\bar{U}_2^2}$  be the corresponding values for the other gas. Then:—

$$P = \frac{1}{3}m_1N_1\bar{U}_1^2 = \frac{1}{3}m_2N_2\bar{U}_2^2;$$

$$\therefore m_1N_1\bar{U}_1^2 = m_2N_2\bar{U}_2^2.$$

If the average kinetic energy of the molecules of a gas be taken as a measure of the temperature (Art. 3), the mean kinetic energy of the molecules of the first gas is  $\frac{1}{2}m_1\bar{U}_1^2$ , and of the second  $\frac{1}{2}m_2\bar{U}_2^2$ , so that for the same temperature;

$$\therefore m_1\bar{U}_1^2 = m_2\bar{U}_2^2, \text{ i.e. } N_1 = N_2.$$

Thus, at the same temperature and pressure, equal volumes of all gases contain the same number of molecules. This is *Avogadro's law*.

### 8. Dalton's Law of Pressures

When two or more gases which have no chemical action upon each other, occupy the same space, the pressures exerted by the various constituents of the mixture are given by the expressions,  $\frac{1}{3}m_1N_1\bar{U}_1^2$ ,  $\frac{1}{3}m_2N_2\bar{U}_2^2$ , etc. The total pressure,  $P$ , is therefore:—

$$P = \frac{1}{3}m_1N_1\bar{U}_1^2 + \frac{1}{3}m_2N_2\bar{U}_2^2 + \dots$$

This is an expression of *Dalton's law*, which states that the pressure of a mixture of gases is the sum of the pressures that the individual gases would exert if occupying the same space at the same temperature (page 186).

Since the gases occupying the same space will acquire the same temperature,  $\frac{1}{2}m_1\bar{U}_1^2 = \frac{1}{2}m_2\bar{U}_2^2 = \text{etc.} = \frac{1}{2}m\bar{U}^2$ ;

$$\therefore P = \frac{1}{3}(N_1 + N_2 + \dots) m\bar{U}^2.$$

### 9. Van der Waals' Equation

The kinetic theory of gases outlined above deals only with the case of an ideal gas, and takes no account of two important factors, (1) the actual size of the molecules, (2) the influence of one molecule on another. In the proof of Boyle's law based on this theory (Art. 4) these two factors were omitted from consideration. And

the experiments of **Regnault**, **Amagat**, and others (page 257) showed that Boyle's law does not represent the exact behaviour of a gas under all conditions of temperature and pressure.

Many phenomena, such as that of cohesion, show that the molecules of a gas do have a definite action on each other, especially when they are closely packed, and it is not surprising, therefore, that actual gases exhibit deviations from Boyle's law, especially at high pressures.

The simple kinetic theory can be modified to take account of this effect and be brought into closer agreement with observed results. The first really satisfactory modification was introduced by **Van der Waals** in 1879, and within certain limits the equation established represents the behaviour of gases with sufficient accuracy, though the agreement is not *absolute*.

First, the actual size of the molecule diminishes the space available for movement, and therefore increases the number of collisions of the molecules with the walls of the enclosure. Thus, if  $d$  is the diameter of a molecule, the number of collisions with the wall of the enclosure (see Art. 2) will be  $\frac{x}{2(s-d)}$  per second, instead

of  $\frac{x}{2s}$  per second. The general effect of this may be summed up by saying that the volume available for movement is not the actual volume,  $V$ , of the gas, but  $(V - b)$  where  $b$  is a space *proportional* to the volume occupied by the molecules themselves. This quantity,  $b$ , is not equal to the actual volume of the molecules, but has been shown to be four times this volume.

Secondly, cohesion suggests that there is a force of attraction between the molecules. This force is great when the molecules are close together, but the behaviour of gases shows that the force becomes small when the distance between the molecules is great. In other words, each molecule may be considered to have a sphere of influence of a certain radius, and any molecule which comes within this sphere will suffer attraction. The resultant effect of the mutual attractions of the molecules will be zero, except near the walls of the enclosure. Here, however, the molecules will strike the wall with less force than would otherwise be the case, and the value of the pressure at the wall is reduced. The magnitude of the effect is proportional to the number of molecules; that is, proportional to the density of the gas. It is also proportional to the number of collisions per second with the wall, and this again is

proportional to the density. Thus the *correction* which must be applied is proportional to the square of the density of the gas, and since the density is inversely proportional to the volume, the necessary factor may be written  $\left(P + \frac{a}{V^2}\right)$  where  $a$  is a constant depending on the nature of the gas.

Thus, instead of the simple relation,  $PV = RT$ , Van der Waals' equation is written

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT.$$

### 10. Deviations from Boyle's Law

Van der Waals' equation is a very much closer representation of the observed behaviour of gases than the simple equation,  $PV = RT$ . A simple consideration of the equation will show how it takes into account the observed deviations from Boyle's law (page 257). As far as these deviations are concerned, it should be noticed that the two effects used in establishing the equation (Art. 9) operate in opposite directions.

In the first place, suppose that instead of using the relation,  $PV = a$  constant, the first effect only is taken into consideration, and the relation is written

$$P(V - b) = \text{constant}.$$

$$\text{Hence, } PV = Pb + \text{constant}.$$

*From this, it is evident that PV increases with pressure.*

Secondly, suppose that the second effect only is considered, and the relation is written

$$\left(P + \frac{a}{V^2}\right)V = \text{constant}.$$

$$\text{Hence, } PV = \text{Constant} - \frac{a}{V}.$$

*From this, it is evident that PV diminishes as V diminishes, or as P increases.*

The actual behaviour of the gas will depend on which of the two effects is of more importance. In the case of gases such as air and nitrogen, the effect of the molecular attraction is predominant at first and PV diminishes with pressure. When, however, the compression is great, the size of the molecules compared with the total

volume of the gas becomes the predominant factor, and  $PV$  increases (see Fig. 163). In the case of hydrogen, with which  $PV$  increases with pressure (see Fig. 162), the attraction between the molecules is of small effect compared with the other factor.

## 11. The Critical Constants

If a series of graphs, connecting  $P$  and  $V$  for a series of constant temperatures and using Van der Waals' equation, is plotted, a number of *isothermals* of the type shown (Fig. 223) is obtained. A comparison of this curve with those of Fig. 157 shows at once that there is a similarity. Van der Waals' equation being continuous, there will be no sudden changes as in the isothermal for carbon dioxide at  $21.5^\circ \text{C}$ . (Fig. 157); but if a straight line,  $ACB$  (Fig. 223), is drawn, such that the areas cut off above and below it are equal, the similarity becomes much more obvious.

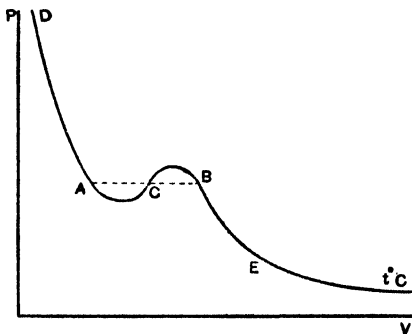


FIG. 223.

$$\text{The equation, } \left(P + \frac{a}{V^2}\right)(V - b) = RT,$$

$$\text{may be written } (PV^2 + a)(V - b) = RTV^2,$$

$$\text{or, } PV^3 - (bP + RT)V^2 + aV - ab = 0,$$

$$\text{or, } V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{aV}{P} - \frac{ab}{P} = 0,$$

which is a cubic equation having three values of  $V$  corresponding to one value of  $P$ , such as  $A$ ,  $C$ ,  $B$  (Fig. 223).

As the temperature is increased, the line,  $AB$  (Fig. 223), decreases until the points,  $A$ ,  $C$ ,  $B$ , coincide in one point—the critical point—such as the point  $C$  (Fig. 157). But in this case, the values of  $P$  and  $T$  must be such that the equation is in the form of a perfect cube—that is, it must satisfy the condition that

$$(V - V_c)^3 = 0;$$

$$\therefore V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0,$$

where  $V_c$  denotes the *critical volume*. The values of  $P$  and  $T$  are then the *critical pressure*,  $P_c$ , and the *critical temperature*,  $T_c$ . Then:—

$$V^3 - \left(b + \frac{RT_c}{P_c}\right) V^2 + \frac{aV}{P_c} - \frac{ab}{P_c} = 0.$$

Equating coefficients of like powers of  $V$ :—

$$3V_c = b + \frac{RT_c}{P_c}; \quad 3V_c^2 = \frac{a}{P_c}; \quad V_c^3 = \frac{ab}{P_c},$$

from which it may be obtained that

$$\begin{aligned} V_c &= 3b, \\ P_c &= \frac{a}{27b^2}, \\ T_c &= \frac{8a}{27Rb}. \end{aligned}$$

Thus it is seen that there is a definite relation between the *critical constants* of a gas and the values of the constants,  $a$  and  $b$ , of Van der Waals' equation. The values of  $a$  and  $b$  can be deduced from observations on the compressibility of a gas, such as those of **Amagat** (page 260), and, using these values, the critical constants can be calculated.

## 12. Relation Between the Ratio of the Specific Heats of a Gas and its Structure

It was shown above (Art. 2) that for a perfect gas,  $PV = \frac{1}{3}mN\bar{U}^2 = \frac{1}{3}M\bar{U}^2$ , where  $M$  is the mass of the gas. This may be written,  $PV = \frac{2}{3}(\frac{1}{2}M\bar{U}^2)$ . But,  $\frac{1}{2}M\bar{U}^2$  is the kinetic energy of the molecules of the gas.

Dealing with unit mass of the gas at an absolute temperature of  $T^\circ$ , and using the characteristic equation of a perfect gas, then:—

$$PV = RT = \frac{1}{3}\bar{U}^2,$$

and therefore, the kinetic energy of translation of the molecules of unit mass of gas is given by:—

$$\frac{\bar{U}^2}{2} = \frac{3}{2}RT.$$

Suppose now the temperature of the gas is raised by  $1^\circ$ . The new kinetic energy of translation of the molecules  $= \frac{3}{2}R(T + 1)$ , and the increase of energy is given by:—

$$\text{Increase of energy} = \frac{3}{2}R(T + 1) - \frac{3}{2}RT = \frac{3}{2}R.$$

In this treatment of the gas on the basis of the kinetic theory, it has been assumed that the molecules are merely infinitesimally small particles, and that the only energy the molecules can have is kinetic energy of translation. If, however, the molecules are not simple particles of infinitesimal size, kinetic energy other than that of translation will have to be taken into account. For example, if a molecule consists of a group of atoms, the group will most probably have a certain amount of rotational movement, and, in that case, when the temperature is raised the kinetic energy of rotation will probably increase as well as that of translation.

Let  $e$  denote the increase in the energy of rotation produced by an increase of temperature of  $1^\circ \text{A}$ . Then, the total energy imparted to 1 grm. of gas to raise its temperature  $1^\circ \text{A}$ . at *constant volume* is:—

$$\frac{3}{2}R + e = S_v, \text{ the specific heat at constant volume.}$$

It has been shown (page 241) that the specific heat of a gas at constant pressure,  $S_p$ , is greater than that at constant volume,  $S_v$ , by the amount of mechanical work done against the external pressure owing to the rise of temperature of  $1^\circ$ , when the gas is allowed to expand at constant pressure. That is:—

$$S_p - S_v = PV = R,$$

$$\text{i.e. } S_p = S_v + R;$$

$$\therefore S_p = \frac{3}{2}R + e + R = \frac{5}{2}R + e,$$

and the ratio of the two specific heats of the gas is:—

$$\gamma = \frac{S_p}{S_v} = \frac{\frac{5}{2}R + e}{\frac{3}{2}R + e};$$

$$\therefore \gamma - 1 = \frac{(\frac{5}{2}R + e) - (\frac{3}{2}R + e)}{\frac{3}{2}R + e} = \frac{R}{\frac{3}{2}R + e},$$

$$\text{or } \frac{n}{2}(\gamma - 1) = \frac{\frac{3}{2}R}{\frac{3}{2}R + e},$$

$$\text{i.e. } \frac{n}{2}(\gamma - 1) = \frac{\text{Increase of energy of translation of molecules per } 1^\circ}{\text{Increase of total energy of molecules per } 1^\circ}.$$

It can be shown that this ratio is equal to  $\frac{3}{n}$ , where  $n$  is called the number of *degrees of freedom* of the molecule. For any given system, the number of degrees of freedom is equal to the number of co-ordinates required to define the position of the elements of the



system, less the number of independent relations existing between them. Thus:—

$$\frac{3}{2}(\gamma - 1) = \frac{3}{n}; \quad \therefore \gamma = 1 + \frac{2}{n}.$$

For monatomic gases, such as argon, helium, etc.,  $n = 3$ , and  $\gamma = \frac{5}{3} = 1.67$ .

For diatomic gases, such as hydrogen, oxygen, nitrogen, etc.,  $n = 5$ , and  $\gamma = \frac{7}{5} = 1.40$ .

For triatomic gases, such as carbon dioxide, water vapour, etc.,  $n = 7$ , and  $\gamma = \frac{9}{7} = 1.29$ .

The values thus obtained agree fairly well with those obtained experimentally in the case of the simpler gases, but the agreement is not so good in the case of the more complex molecules.

### 13. Internal and External Work in Change of State

When change of state occurs with change of volume (see pages 131, 153), the heat required to produce the change consists of two parts, (1) the equivalent of the external work done while the volume of the substance changes, and (2) the equivalent of the work done in changing the internal energy of the molecules of the substance. For example, in the change of state from liquid to vapour, there is a large increase of volume, and therefore when a liquid boils the vapour has to do work against the atmosphere. The question arises: How much of the latent heat of vaporisation is used to increase the molecular energy of the substance, and how much is spent in doing work against the atmosphere?

**Example.**—1 grm. of water at  $100^{\circ}\text{C}$ . occupies a volume of 1.043 c.c., and 1 grm. of steam occupies at  $100^{\circ}\text{C}$ . and normal atmospheric pressure, 760 mm. of mercury, a volume of 1672.5 c.c. If the transformation takes place under a uniform pressure, the work done is given by the product of the pressure and the change of volume.

The pressure is  $76 \times 13.596 \times 981$  dynes per sq. cm.

The change of volume is  $1672.5 - 1.04 = 1671.46$  c.c.

Hence, the work done is  $1671.46 \times 76 \times 13.596 \times 981$  ergs, and the heat equivalent of this external work is—

$$\frac{1671.46 \times 76 \times 13.596 \times 981}{4.19 \times 10^7} = 40.21 \text{ calories.}$$

Therefore, of the 540 calories which are required to convert 1 grm. of water at  $100^{\circ}\text{C}$ . into 1 grm. of steam at  $100^{\circ}\text{C}$ ., 40 calories are spent in doing external work and the balance of 500 calories on increasing the energy of the molecules. Other cases of vaporisation may be treated in the same way.

## EXERCISES

### EXERCISES II

1. Mercury freezes at  $-40^{\circ}\text{C}$ . What is the corresponding temperature on the Fahrenheit scale?

2. How many Fahrenheit degrees are equal to 20 Centigrade degrees, and what Fahrenheit temperature is the same as  $20^{\circ}\text{C}$ .?

3. Convert the following Centigrade temperatures into their equivalent temperatures on each of the other scales:—

$$850^{\circ}, -6^{\circ}, -50^{\circ}\text{C}.$$

4. Convert the following Fahrenheit temperatures into their equivalent temperatures on each of the other scales:—

$$230^{\circ}, 27^{\circ}, -10^{\circ}, -49^{\circ}\text{F}.$$

5. Convert the following Réaumur temperatures into their equivalent temperatures on each of the other scales:—

$$110^{\circ}, -8^{\circ}, -27^{\circ}\text{R}.$$

6. A Centigrade thermometer was calibrated with the following results:—

(a) Assuming the  $0^{\circ}\text{C}$ . and  $100^{\circ}\text{C}$ . points to be correct, the following table gives the corrections at the enumerated temperatures:—

$10^{\circ}$	$20^{\circ}$	$30^{\circ}$	$40^{\circ}$	$50^{\circ}$	$60^{\circ}$	$70^{\circ}$	$80^{\circ}$	$90^{\circ}$
+ 0.12	+ 0.24	+ 0.72	+ 0.23	+ 0.12	+ 0.10	+ 0.08	+ 0.06	+ 0.06

(b) The correction at  $0^{\circ}\text{C}$ . was  $-0.20^{\circ}$ , the correction at  $100^{\circ}\text{C}$ . was  $-0.62^{\circ}$ .

Plot a graph between correction and temperature, and find the corrections at  $25^{\circ}\text{C}$ .,  $45^{\circ}\text{C}$ .,  $85^{\circ}\text{C}$ .

### EXERCISES III

1. The resistance of a platinum thermometer in melting ice is 592.387 units, and in steam at  $100^{\circ}\text{C}$ . it is 821.922 units. What is the temperature when its resistance is exactly 640 units?

2. The resistance of a platinum thermometer was measured in melting ice ( $0^{\circ}\text{C}$ .), steam ( $99.9^{\circ}\text{C}$ .), and sulphur vapour ( $444.4^{\circ}\text{C}$ .), and was found to be 347.1, 451.6, and 784.8 units respectively. Express the ratio  $\frac{R_t}{R_0}$  as a formula  $1 + at + bt^2$ , and find the value of  $\delta$  for this particular thermometer.

### EXERCISES IV

Where the coefficients of expansion are not quoted, use Table II, page 394.

1. The coefficient of linear expansion of brass is 0.000019. What will be the volume at  $100^{\circ}\text{C}$ . of a mass of brass the volume of which is exactly 1 c.dm. at  $0^{\circ}\text{C}$ .?

2. The coefficient of linear expansion of brass is  $0.00018$ . If a brass yard measure is correct at the temperature of melting ice, what will be its error at the temperature of boiling water?

3. A light lath, 1 m. long, can turn about a hinge at one end. A piece of wire, 2 m. long, is attached to the lath at a distance of 1 cm. from the hinge. The wire is vertical and its upper end is fixed so that the lath is horizontal. On heating the wire  $50^{\circ}\text{C}$ . the free end of the lath sinks through 16 cm. Find the coefficient of linear expansion of the material of the wire.

4. A brass rod and a steel rod are each 1 m. long at  $10^{\circ}\text{C}$ . Find the difference in their lengths at  $60^{\circ}\text{C}$ .

5. The volume of a piece of glass at  $100^{\circ}\text{C}$ . is 100.258 c.c. and its volume at  $0^{\circ}\text{C}$ . is 100 c.c. Find the mean coefficient of cubical expansion of glass between  $0^{\circ}\text{C}$ . and  $100^{\circ}\text{C}$ ., and thence deduce approximately the mean coefficient of linear expansion between the same limits of temperature.

6. A sphere of glass at  $40^{\circ}\text{C}$ . is lowered into a vessel full of water at  $40^{\circ}\text{C}$ . and one pint of water overflows. Find what quantity will overflow if the same sphere at  $100^{\circ}\text{C}$ . is placed in a vessel full of water at  $100^{\circ}\text{C}$ . The coefficient of cubical expansion of glass is  $0.000025$ .

7. Find the mass of 1 c.c. of silver at  $250^{\circ}\text{C}$ ., the density of silver at  $0^{\circ}\text{C}$ . being 10.31 gm. per c.c.

8. Compare the densities of platinum and silver at  $100^{\circ}\text{C}$ ., given that the densities of the metals at  $0^{\circ}\text{C}$ . are 21.500 and 10.570 gm. per c.c. respectively.

### EXERCISES V

1. The coefficient of absolute expansion of mercury being  $\frac{1}{273}$  and its coefficient of apparent expansion in glass being  $\frac{1}{8480}$ , find the coefficient of cubical expansion of glass.

2. A zinc rod is measured by means of a brass scale and its length at  $10^{\circ}\text{C}$ . is found to be 1.0001 m. Find the true length of the rod at  $0^{\circ}\text{C}$ . and at  $10^{\circ}\text{C}$ .

3. A rod of copper and a rod of iron placed side by side are riveted together at one end. The iron rod is 150 cm. long, and a mark is made on the copper rod, showing the position of the free end of the iron rod at  $0^{\circ}\text{C}$ . If at  $30^{\circ}\text{C}$ . the mark is 0.025 cm. from the end of the iron rod, find the coefficient of expansion of copper.

4. A glass weight thermometer weighs 1.3210 gm. when empty. After filling it with mercury at  $0^{\circ}\text{C}$ . and then heating it to  $100^{\circ}\text{C}$ ., 0.2351 gm. of mercury was expelled. The weight thermometer with the residue of the mercury, when cooled to the temperature of the atmosphere, weighed 16.3075 gm. Calculate the coefficient of apparent expansion of mercury and the coefficient of cubical expansion of glass.

5. A glass weight thermometer weighs 1.3210 gm. when empty. After filling it with glycerin at  $0^{\circ}\text{C}$ . and then heating to  $100^{\circ}\text{C}$ ., 0.0678 gm. of glycerin was expelled. On cooling down the total weight was 2.710 gm. If the coefficient of cubical expansion of glass is 0.000025, find the coefficient of absolute expansion of glycerin.

6. A porcelain weight thermometer weighs 165 gm. when empty and 468 gm. when full of mercury at  $0^{\circ}\text{C}$ . When heated to  $300^{\circ}\text{C}$ ., 13.464 gm. of mercury overflowed. Find the mean coefficient of cubical expansion of porcelain between  $0^{\circ}\text{C}$ . and  $300^{\circ}\text{C}$ ., assuming that of mercury to be 0.000184 for the same range of temperature.

7. An empty weight thermometer weighed 4.8155 gm. It was filled with water at  $10^{\circ}\text{C}$ . and heated gradually in a bath. It was withdrawn and weighed at  $20^{\circ}$ ,  $40^{\circ}$ ,  $60^{\circ}$ ,  $80^{\circ}$ ,  $95^{\circ}\text{C}$ ., the weights being 23.9032, 23.7966, 23.6340, 23.4220, and 23.2376 gm. Find the coefficient of real expansion of water between  $20^{\circ}$  and  $40^{\circ}$ ,  $40^{\circ}$  and  $60^{\circ}$ ,  $60^{\circ}$  and  $80^{\circ}$ ,  $80^{\circ}$  and  $95^{\circ}\text{C}$ . Plot a graph showing the change of the coefficient with temperature.

8. The coefficient of absolute expansion of mercury is 0.00018, the coefficient of linear expansion of glass is 0.00008. Mercury is placed in a graduated glass tube and occupies 100 divisions of the tube. Find the change of temperature necessary to cause the mercury to occupy 101.56 divisions.

9. A mercury thermometer wholly immersed in boiling water reads  $100^{\circ}\text{C}$ . When the stem is withdrawn, so that the graduations from  $0^{\circ}$  upwards are at an average temperature of  $10^{\circ}\text{C}$ ., the reading is  $98.6^{\circ}\text{C}$ . Find the coefficient of apparent expansion of mercury in glass.

10. A piece of glass weighs 47 gm. in air, 31.53 gm. in water at  $4^{\circ}\text{C}$ ., and 31.75 gm. in water at  $60^{\circ}\text{C}$ . Find the mean coefficient of expansion of water between  $4^{\circ}$  and  $60^{\circ}\text{C}$ ., assuming the coefficient of cubical expansion of glass to be 0.000024.

11. A solid weighs 45.6 gm. in air, 29.9 gm. in a liquid of specific gravity 1.21 at  $10^{\circ}\text{C}$ ., and 30.4 gm. in the same liquid at  $95^{\circ}\text{C}$ . when the specific gravity is 1.17. Find the coefficient of cubical expansion of the solid.

12. In an experiment to find the expansion of aniline, using Dulong and Petit's apparatus, the column at  $0^{\circ}\text{C}$ . was 62.3 cm. high, and the column at  $100^{\circ}\text{C}$ . was 5.67 cm. higher. Find the coefficient of real expansion of aniline.

13. In an experiment to find the coefficient of absolute expansion of mercury by Regnault's method, the following data were obtained:  $H = 100$  cm.,  $h_1 = 12.4$  cm.,  $h_2 = 15.97$  cm.,  $t_1 = 10^{\circ}\text{C}$ .,  $t_2 = 210^{\circ}\text{C}$ . Find the value of  $c_r$  given by this experiment.

14. A barometer is provided with a silver scale which reads correctly at  $0^{\circ}\text{C}$ . and reads 761.05 mm. at  $15^{\circ}\text{C}$ . Find the true barometric reading. Also find the reading corrected to  $0^{\circ}\text{C}$ .

## EXERCISES VI

1. A litre of hydrogen at  $10^{\circ}\text{C}$ . is heated at constant pressure to  $293^{\circ}\text{C}$ . Find its volume.

2. Air is enclosed in a vessel at  $0^{\circ}\text{C}$ . and, the volume being kept constant, the temperature is reduced to  $-88^{\circ}\text{C}$ ., at which temperature the pressure is found to be 385 mm. Find the pressure at  $0^{\circ}\text{C}$ .

3. Find the volume occupied at  $0^{\circ}\text{C}$ . and 760 mm. pressure by 500 c.c. of oxygen measured at  $10^{\circ}\text{C}$ . and 750 mm. pressure.

4. 1000 c.c. of air at  $50^{\circ}\text{C}$ . are cooled to  $10^{\circ}\text{C}$ . and at the same time the external pressure upon the air is increased from 750 mm. to 765 mm. Find the new volume of the air.

5. In a determination of the coefficient of expansion of air by Gay-Lussac's method, the volume of air in the tube was found to be 240 c.c. at  $0^{\circ}\text{C}$ . and at  $77^{\circ}\text{C}$ . its apparent volume was 310 c.c. If the coefficient of cubical expansion of glass is 0.000026, find the value obtained for the required coefficient.

6. A porcelain air thermometer is used to determine the temperature of a furnace. The excess pressure of the air in the bulb over the atmospheric pressure is found to be equal to 1843 mm. of mercury. Find the temperature of the furnace, given that the barometric height at the time of determination is 758 mm., and that at  $0^{\circ}\text{C}$ . the pressure of the air in the bulb is equal to that of the atmosphere.

7. A litre of hydrogen weighs 0.09 grm. at  $0^{\circ}\text{C}$ . and 760 m.m. pressure. Find the weight of a litre at  $20^{\circ}\text{C}$ . and 766 mm. pressure.

8. Compare the density of air at  $10^{\circ}\text{C}$ . and 750 mm. pressure with its density at  $15^{\circ}\text{C}$ . and 760 mm. pressure.

9. A flask containing air is corked at  $20^{\circ}\text{C}$ . and heated in an air bath. A pressure of 2 atmospheres inside the flask will force the cork out. Find the temperature at which this occurs.

10. Find the temperature of the absolute zero on the Fahrenheit scale.

11. 500 c.c. of oxygen are measured at  $20^{\circ}\text{C}$ . and the temperature is raised to  $40^{\circ}\text{C}$ ., the pressure remaining unchanged. Find the volume of the oxygen at the latter temperature.

12. 1000 cub. in. of air at a temperature of  $30^{\circ}\text{C}$ . are cooled to  $0^{\circ}\text{C}$ . and at the same time the external pressure upon the air is doubled. Find the new volume of the air.

#### EXERCISES VII

1. If the specific heat of iron is  $\frac{1}{8}$  and 1 lb. of iron is cooled from the temperature of boiling water to the temperature of melting ice, how many units of heat are evolved?

2. 10 grm. of water at  $98^{\circ}\text{C}$ . are poured into a copper vessel weighing 25 grm. and containing 100 grm. of water at  $6^{\circ}\text{C}$ . If the specific heat of copper is 0.092, find the final temperature of the mixture.

3. Equal volumes of two liquids, A and B, are mixed. The specific gravity of A is 1.8, and of B, 0.56; the specific heat of A is 0.3, and of B, 0.6; the temperature of A is  $60^{\circ}\text{C}$ ., and of B,  $40^{\circ}\text{C}$ . Find the final temperature.

4. A piece of silver weighing 21 grm. is heated to  $98^{\circ}\text{C}$ . and dropped into a calorimeter containing 100 grm. of water at  $10^{\circ}\text{C}$ . The water equivalent of the calorimeter is 3.6 grm. and the final temperature is  $11^{\circ}\text{C}$ . Find the specific heat of silver.

5. 10 grm. of common salt at  $91^{\circ}\text{C}$ . having been immersed in 125 grm. of turpentine at  $13^{\circ}\text{C}$ ., the temperature of the mixture was  $16^{\circ}\text{C}$ . Taking the specific heat of turpentine as 0.428, find the specific heat of common salt.

6. 200 grm. of copper of specific heat 0.095 are heated to  $100^{\circ}\text{C}$ . and placed in 100 grm. of alcohol at  $8^{\circ}\text{C}$ . contained in a copper calorimeter weighing 25 grm., and the temperature rises to  $28.5^{\circ}\text{C}$ . Find the specific heat of alcohol.

7. Find the water equivalent of a calorimeter from the following experimental data: Weight of calorimeter, 45.623 grm.; weight of calorimeter and water, 224.583 grm.; initial temperature of calorimeter and water,  $9^{\circ}\text{C}$ . Temperature of hot water,  $78^{\circ}\text{C}$ . Final temperature,  $13.2^{\circ}\text{C}$ . Weight of calorimeter after addition of hot water, 236.493 grm.

8. A sphere of platinum of specific heat, 0.031, and weighing 200 grm. is removed from a furnace and immersed in 150 grm. of water at  $0^{\circ}\text{C}$ . The temperature of the water rises to  $30^{\circ}\text{C}$ . Assuming that the water gains all the heat lost by the platinum, find the temperature of the furnace.

9. Find the specific heat of bronze from the following experimental data: Weight of bronze, 21.3 gm. Weight of calorimeter, 52.97 gm.; specific heat of copper, 0.095; weight of water in calorimeter, 105.73 gm. Initial temperature of bronze, 99.5° C.; initial temperature of water and calorimeter, 17° C. Final temperature of mixture, 18.5° C.

10. Find the specific heat of alcohol from the following experimental data: Weight of copper dropped into calorimeter, 10 gm.; weight of copper calorimeter, 20.4 gm.; weight of calorimeter and alcohol, 70.5 gm. Initial temperature of copper, 98° C.; initial temperature of calorimeter and alcohol, 10° C. Final temperature of mixture, 12.6° C.

11. Regnault found that 100.5 units of heat were required to raise the temperature of unit mass of water from 0° C. to 100° C., and 203.2 units to raise its temperature to 200° C. Find the mean specific heat of water between 0° C. and 100° C., between 100° and 200° C., and between 0° C. and 200° C.

12. 9 gm. of hydrogen at 0° C. were heated to 210° C. and then passed through a calorimeter of water equivalent 5 gm., and containing 500 gm. of water. The temperature was initially 10° C. and finally 22° C., and it was estimated that 36 calories were lost by cooling during the passage of the gas. Find the specific heat of hydrogen.

13. Find the mean specific heat of turpentine from the following experimental data, obtained by the method of cooling: Weight of calorimeter (copper), 38 gm.; weight of calorimeter with turpentine, 87.4 gm.; with water, 94.7 gm. Times of cooling for successive 5° C. from 70° C. to 55° C., 80, 92, and 105 sec. with turpentine; 179, 201, and 233 sec. with water. Specific heat of copper, 0.095.

14. The specific heat of iron is 0.114. Find its approximate atomic weight.

### EXERCISES VIII

1. Assuming the specific heat of lead to be 0.031, and its latent heat 5.07, find the quantity of heat required to raise the temperature of 15 gm. of lead from 115° C. to its melting point, 320° C., and to melt it.

2. 10 gm. of ice at -10° C. are mixed with 120 gm. of water at 80° C. Find the final temperature. The specific heat of ice is 0.47.

3. Find the latent heat of fusion of ice from the following experimental data: Weight of brass calorimeter, 35 gm.; weight of calorimeter and water, 156 gm.; specific heat of brass, 0.09. Initial temperature of water and calorimeter, 24° C.; final temperature, 17° C. Weight of calorimeter, etc., after addition of ice, 165 gm.

4. 500 c.c. of mercury at 56° C. are put into a cavity in a block of ice, and it is found that 159 gm. of ice are melted. Find the specific heat of mercury. The density of mercury is 13.6 gm. per c.c.

5. If 100 c.c. of water at 0° C. become 109 c.c. of ice at 0° C., find the quantity of heat required to cause a mixture of ice and water to contract by 50 c.c.

6. 1 gm. of ice at 0° C. contracts 0.091 c.c. in becoming water at 0° C. A piece of metal weighing 10 gm. is heated to 50° C. and then dropped into a Bunsen ice calorimeter. The total contraction is 0.063 c.c. Find the specific heat of the metal.

7. 10 gm. of water at 96° C. are placed in a Bunsen ice calorimeter, and it is found that the volume of the contents of the outer portion of the calorimeter decreases by 1.09 c.c. Find the specific gravity of ice.

8. If 100 c.c. of water in freezing become 109 c.c. of ice, and if the introduction of 20 grm. of mercury at  $100^{\circ}\text{C}$ . into a Bunsen ice calorimeter causes the end of the mercury column to move through 74 mm. in a tube of cross-section 1 sq. mm., find the specific heat of mercury.

## EXERCISES IX

1. The boiling point of water on the top of a mountain is found to be  $89^{\circ}\text{C}$ . What would be the height of a barometer there? Express the pressure in dynes per sq. cm. (Take  $g = 980$ .)

2. Into 200 grm. of water at  $20^{\circ}\text{C}$ . are placed 100 grm. of pounded ice at  $0^{\circ}\text{C}$ . Steam is then passed into the mixture until all the ice has melted and the temperature of the water is again  $20^{\circ}\text{C}$ . The increase of weight is found to be 16.2 grm. Find the latent heat of vaporisation of water.

3. 50 grm. of steam at  $100^{\circ}\text{C}$ . are passed into a mixture of 100 grm. of ice and 200 grm. of water at  $0^{\circ}\text{C}$ . The water equivalent of the vessel containing the mixture of water and ice is 15 grm. Find the rise of temperature produced.

4. Find the latent heat of steam at  $100^{\circ}\text{C}$ . from the following data: Weight of calorimeter, 105 grm.; weight of calorimeter and water, 346 grm.; final weight of calorimeter and contents, 354.16 grm.; water equivalent of calorimeter, 9 grm. Initial temperature of calorimeter and water,  $4^{\circ}\text{C}$ .; final temperature,  $24^{\circ}\text{C}$ . Height of barometer, 752 mm. (The steam is produced at atmospheric pressure.)

5. 10 grm. of steam at  $60^{\circ}\text{C}$ . are passed into 600 grm. of water at  $4^{\circ}\text{C}$ . The final temperature of the mixture is  $14.18^{\circ}\text{C}$ . Find the latent heat of steam at  $60^{\circ}\text{C}$ . Verify by Regnault's relation.

6. Find the quantity of heat required to vaporise 10 grm. of alcohol at  $78.3^{\circ}\text{C}$ . The latent heat of alcohol at  $78.3^{\circ}\text{C}$ . is 202.

7. 20 grm. of ether vapour at  $35^{\circ}\text{C}$ . are passed into 100 grm. of ether at  $0^{\circ}\text{C}$ . in a copper vessel weighing 12.5 grm. Find the final temperature. The specific heat of ether is 0.53 and the latent heat at  $35^{\circ}\text{C}$ . is 90.5.

8. Find the specific heat of quartz from the following observations with the steam calorimeter: 16.73 grm. of quartz were placed in the chamber at  $15.25^{\circ}\text{C}$ . Steam at  $100.5^{\circ}\text{C}$ . was passed into the chamber and the water condensed by the quartz weighed 0.497 grm.

## EXERCISES X

(See Table XIII., page 398.)

1. A closed vessel is filled with dry air at a temperature of  $15^{\circ}\text{C}$ . and a pressure of 763.7 mm. of mercury. Without allowing any of the air to escape, it is saturated with moisture. The temperature is now raised to  $25^{\circ}\text{C}$ . Find the total pressure.

2. A quantity of hydrogen is collected over water in a eudiometer tube. The height of the column of water left in the tube is 40.8 mm., and its temperature is  $15^{\circ}\text{C}$ . The barometric height is 758 mm., and the hydrogen is saturated with aqueous vapour. Find the pressure of the hydrogen.

3. A quantity of dry air measures 1000 c.c. at  $10^{\circ}\text{C}$ . and 760 mm. pressure. If the same quantity of air is heated to  $30^{\circ}\text{C}$ . and saturated with aqueous vapour at that temperature, what must be the volume of the moist air, in order that the pressure may remain unchanged?

4. A bubble containing 0.01293 mgm. of air is formed 136 mm. below the surface of water at 80° C. Find its volume. The barometric height is 750 mm.; 1 c.c. of air weighs 1.293 mgm. at 0° C. and 760 mm. pressure.

5. If the maximum pressure of water vapour is 758 mm. at 99.93° C. and 759 mm. at 99.96° C., what increase in size takes place in a bubble of air just under the surface of water as the temperature rises from 99.93° C. to 99.96° C., supposing the pressure of the atmosphere to be 760 mm.? What further increase would take place as the temperature rises from 99.96° C. to 100° C.?

6. A bubble of air is formed 68 mm. below the surface of water at 10° C. How many bubbles of volume equal to its own will this bubble give rise to when the temperature rises to 90° C.? The barometric height is 760 mm.

7. Calculate the molecular weight of water from the following data obtained by Gay-Lussac's method: Weight of water, 0.0392 gm. Temperature of bath, 100.5° C. Barometric height, 753.4 mm. Height of mercury column (at 100.5° C.), 235.5 mm. Volume of water vapour, 95.7 c.c.

8. Calculate the molecular weight of chloroform from the following data obtained by Dumas' method: Capacity of bulb, 127 c.c. Temperature of bath, 136° C. Weight of vapour, 0.4524 gm.

9. Calculate the molecular weight of a substance from the following data obtained by Victor Meyer's method: Weight of liquid, 0.027 gm. Volume of air collected, 11.1 c.c. at 11° C. and a total pressure of 33 ft. of water. Atmospheric pressure, 34 ft. of water.

### EXERCISES XI

1. Two cubic metres of air at 17° C. were drawn through an absorption hygrometer, and 24.12 gm. of water were deposited in the tubes. Find the relative humidity of the air.

2. Find the hygrometric state of the air at 20° C., the dew-point being 10° C.

3. Find the dew-point when the relative humidity at 26.4° C. is 20 per cent.

4. Find the mass of a litre of moist air at 18° C., the dew-point being 5° C. and the barometric height 757.5 mm.

5. 200 c.c. of hydrogen, measured at 15° C. and 754.7 mm. pressure, are collected over water. Find the mass of the hydrogen present. 1 litre of hydrogen at 0° C. and 760 mm. pressure weighs 0.09 gm.

6. 100 c.c. of oxygen, saturated with water vapour, are collected at 15° C. and 740 mm. pressure. Find the volume of dry oxygen at 0° C. and 760 mm. pressure, given that the maximum pressure of aqueous vapour at 15° C. is 12.7 mm. of mercury.

### EXERCISES XII

1. Describe the transformations through which energy passes as clouds are formed and as rain returns from them to the earth.

2. Describe the passage of energy from the coal to the passengers and the rails when a train is in motion.

3. What is meant by the mechanical equivalent of heat? In what sense can it be called the specific heat of water in mechanical units?

4. A mass of 10 lb. falls to the ground from a height of 700 ft. Assuming that it does not rebound, find the heat liberated by impact on the ground.



5. A waterfall is 1400 feet high. Assuming that no energy is lost by the water, find how much hotter the water at the bottom is than that at the top. Express the result on both the Centigrade and the Fahrenheit scales.

6. 1 lb. of lead is raised 20 ft. and dropped upon a stone slab. This is done quickly 10 times, and the lead is found to have been heated  $4.65^{\circ}\text{C}$ . above its initial temperature. Assuming that all the heat generated remains in the lead, and that the specific heat of lead is 0.031, calculate the work equivalent of the heat which would warm 1 lb. of water  $1^{\circ}\text{C}$ .

7. An engine consumes 3 lb. of coal per H.-P. per hr. The heat developed by the combustion of 1 lb. of coal is capable of converting 15 lb. of water at  $100^{\circ}\text{C}$ . into steam at  $100^{\circ}\text{C}$ . Find the efficiency of the engine.

8. A 10 H.-P. engine does 330,000 ft. lb. of work per min. Assuming that only 1 per cent. of the energy in the coal is utilised for mechanical purposes, and that 1 lb. of coal generates 12,000,000 ft. lb. of work during combustion, find the mass of coal used per hr.

9. The specific heat of ice is 0.5. Express this in (a) ft. lb., (b) ergs.

10. Express the latent heat of fusion of ice and the latent heat of vaporisation of water in ft. lb. and in ergs.

11. How may the amount of work done against external pressure during change of volume be expressed numerically? 1 grm. of air is heated under constant pressure from  $0^{\circ}$  to  $10^{\circ}\text{C}$ . Determine the work, in *ergs* and in *grm.-cm.*, due to the expansion.

12. Given that the ratio of the two specific heats of air is 1.41, and that the work done during expansion, at normal pressure, by 1 grm. of air when its temperature is raised from  $0^{\circ}$  to  $1^{\circ}\text{C}$ . is 2930 grm.-cm., find the values of the two specific heats.

13. If a current of 2 amperes flowing in a wire immersed in 100 grm. of water raises the temperature of the water by  $6^{\circ}\text{C}$ . in 20 min., find the resistance of the wire.

### EXERCISES XIII

1. A volume of 100 c.c. of air at  $0^{\circ}\text{C}$ . and 760 mm. pressure is suddenly compressed to half its volume. Find the pressure exerted. The temperature of the gas is then reduced to  $0^{\circ}\text{C}$ . Find the pressure now which is necessary to keep the volume at 50 c.c. ( $\gamma = 1.40$ .)

2. A quantity of air at  $0^{\circ}\text{C}$ . and 1 atmosphere pressure is suddenly compressed to one-tenth its original volume. Find the momentary temperature and pressure at the end of the process.

3. A quantity of air at  $15^{\circ}\text{C}$ . expands adiabatically to twice its volume. Find the temperature at the end of the process.

4. Find the adiabatic change in the volume of a gas in order to reduce its temperature from  $15^{\circ}\text{C}$ . to  $0^{\circ}\text{C}$ . Find also the corresponding change in pressure.

5. Given that the specific heat of air at constant pressure is 0.238, the ratio of the specific heats 1.4, and the density 0.00129 grm. per c.c. at  $0^{\circ}\text{C}$ . and one million dynes per sq. cm. pressure, calculate the mechanical equivalent of heat.

6. The volume of 1 grm. of hydrogen at  $0^{\circ}\text{C}$ . and 760 mm. pressure is 11.16 litres. The velocity of sound in the gas under the same conditions is 1260 m. per sec. If the density of mercury is 13.596 grm. per c.c. and the

mechanical equivalent of heat is  $4.184 \times 10^7$  ergs per calorie, find the specific heats of the gas at constant pressure and at constant volume.

7. Air is pumped into a large vessel fitted with a stopcock and connected to a manometer until the pressure is 36 mm. above that of the atmosphere. The stopcock is then opened suddenly so that the vessel communicates with the atmosphere and is closed again quickly. When conditions are steady, the manometer indicates an excess pressure of 10.5 mm. If the barometric height is 770.3 mm., find the ratio of the specific heats of air.

### EXERCISES XVI

1. Find the quantity of heat that will be transmitted in 1 hr. through a plate of copper 1 sq. m. in area and 5 cm. thick, the difference between the temperatures of its faces being  $10^\circ\text{C}$ . The absolute thermal conductivity of copper is 0.72.

2. It is found that 9,150,000 grm.-degree units of heat are transmitted per minute through a sheet of silver 100 sq. cm. in area and 1 mm. thick with a difference of temperature of  $100^\circ\text{C}$ . between its faces. Find, in c.g.s. units, the thermal conductivity of silver.

3. The quantity of heat which passes in 1 hr. through a plate of lead 1 sq. m. in area and 1 cm. thick, with a difference of  $1^\circ\text{C}$ . between the temperatures of its surfaces, is 1383 kilogram-degree units. Find, in c.g.s. units, the absolute thermal conductivity of lead.

4. How many units of heat will pass through a plate of silver 1 m. long, 1 m. broad, and 5 cm. thick in 1 min., when its opposite faces are kept at temperatures differing by  $100^\circ\text{C}$ . ?

5. The thermal conductivity of felt is 0.000087 c.g.s. units. Find the quantity of heat that is transmitted in 1 hr. through a layer of felt 1 cm. thick and 20 sq. cm. in area, when its opposite faces are kept at temperatures differing by  $20^\circ\text{C}$ .

6. 1 sq. m. of a substance, 1 cm. thick, has one side kept at  $100^\circ\text{C}$ ., and the other at  $0^\circ\text{C}$ ., by means of ice. In 10 min. 1 kgm. of ice is melted by this operation. Find the thermal conductivity of the substance, assuming the latent heat of water to be 80.

7. Express the thermal conductivity of copper in units involving the pound, foot, second, and degree Fahrenheit.

### EXERCISES XVII

1. Define the coefficient of transmission of a substance for radiation. If the coefficient of transmission of a substance for a particular kind of radiation is 0.0012, what percentage of the incident radiation will pass through a plate of the substance 3 mm. thick ?

2. If a plate of glass allowed 40 per cent. of the radiation incident upon it to pass through, how much would be transmitted by a plate of the same glass of four times the thickness, assuming that none is lost by reflection at the surfaces in either case ?

3. If a plate of blue glass 1 mm. thick transmits half the radiation which falls on it from a gaseous sodium flame, what is the coefficient of transmission of the glass ? Does it follow that the plate would transmit half the radiation from a lamp ?

4. A current of steam at atmospheric pressure is passed through an iron tube 2 m. long, internal radius 2.4 cm., and external radius 4 cm. The thermal conductivity of iron is 0.15, the coefficient of emission for the surface of the tube 0.0003, the latent heat of steam 540, and the temperature of the surrounding chamber 0° C. Find the quantity of steam condensed per hour by the cooling effect of the air in the chamber.

### EXERCISES XVIII

1. If the density of nitrogen is 1.25 gm. per litre at normal temperature and pressure, calculate the root mean square velocity of its molecules.

2. Calculate the root mean square velocity of the molecules in the case of a gas whose density is 1.4 gm. per litre at a pressure of 76 cm. of mercury.

3. A perfect gas expands isothermally. If its original volume is 500 c.c., and the pressure changes from 85 cm. to 75 cm. of mercury, find the amount of work done in expansion.

4. Find how much work has to be spent in compressing 1 cub. m. of air at the normal pressure into a vessel of capacity 50 litres.

5. When 1 gm. of water at 100° C. is turned into 1 gm. of steam at 100° C. and atmospheric pressure, the increase of volume is 1671 c.c. The pressure of the atmosphere being  $1.014 \times 10^6$  dynes per sq. cm., find what fraction of the latent heat of vaporisation is spent in doing work against the atmosphere.

6. The latent heat of steam at 100° C. is 536. Find the amount of heat spent in internal work when water at 100° C. is converted into steam at the same temperature, given that 1 kgm. of water when converted into steam at atmospheric pressure occupies a volume of 1.65 cub. m.

## EXAMINATION QUESTIONS

### *Thermometry. Chapters II. and III*

1. Describe a type of thermometer suitable for measuring maximum and minimum atmospheric temperatures. How would you determine any errors of its scale?

2. What are the more important errors likely to affect the accuracy of the indications of a mercury-in-glass thermometer when it is used to determine the temperature of a hot liquid in a beaker? Explain how each of these errors may be allowed for.

Why is mercury commonly used as a thermometric substance?

3. Give an account of platinum resistance thermometry.

4. The resistances of a platinum resistance thermometer at  $0^{\circ}\text{C.}$ ,  $50^{\circ}\text{C.}$ , and  $100^{\circ}\text{C.}$  on the constant volume hydrogen thermometer are given below.

	$0^{\circ}\text{C.}$	$50^{\circ}\text{C.}$	$100^{\circ}\text{C.}$
Resistance	1.2 ohms	1.448 ohms	1.7 ohms.

Find the difference between the temperatures on the Centigrade scales of the platinum resistance thermometer and on the constant volume hydrogen thermometer corresponding to  $50^{\circ}\text{C.}$  on the latter.

Give an account of platinum resistance thermometry and mention any of its advantages.

5. Write a short but detailed essay on electrical thermometers.

6. Describe and explain an electrical method of measuring temperature. How can this method be applied to the measurement of high temperatures?

### *Expansion. Chapters IV. to VI*

7. Define coefficient of thermal expansion, and obtain relations between the coefficients of linear, surface, and volume expansion of an isotropic solid. Describe how you would determine the coefficient of linear expansion of glass.

8. Make a careful drawing of the apparatus you would employ to determine the coefficient of linear expansion of a metal supplied in the form of a rod. Discuss the accuracy of the method.

Show that the coefficient of volume expansion of an isotropic solid is approximately three times that of the coefficient of linear expansion.

9. Describe a good method for measuring the linear coefficient of expansion of the material of a metal rod.

A bar of iron, 5 sq. cm. cross-sectional area, is heated to  $200^{\circ}\text{C.}$ , fixed at both ends and then cooled to  $15^{\circ}\text{C.}$  Calculate the force exerted by the bar on the fixings if Young's modulus for iron is  $2 \times 10^{12}$  dynes per sq. cm. and the coefficient of linear expansion of iron is  $1.2 \times 10^{-6}$  per  $^{\circ}\text{C.}$

10. Define coefficient of linear expansion.

A thin wire, 200 cm long, is stretched horizontally between two clamps and loaded at its centre so that at room temperature ( $15^{\circ}\text{C.}$ ) it is still sensibly straight. It is then heated to  $110^{\circ}\text{C.}$  by an electric current and, in consequence, sags 5 cm. at its centre. What is the coefficient of linear expansion of the metal?

How would you determine the temperature of the wire in this experiment?

11. Describe the comparator method of measuring the linear coefficient of expansion of a material.

An iron wire, 4 m. long at  $15^{\circ}\text{C}$ ., is stretched horizontally between two clamps. When an electric current is passed along the wire, its mid-point descends vertically through 8 cm., the two halves of the wire being kept taut. Calculate the mean rise of temperature of the wire if the coefficient of linear expansion of iron is  $0.000012$  per  $^{\circ}\text{C}$ .

12. Describe two methods which may be applied to determine the small change of length which occurs in the experiment to determine the coefficient of thermal expansion of a metal bar. Explain how the actual change of length of the bar is determined from the observations made.

What volume of iron must be placed in a glass vessel of volume 1 litre in order that the remaining space may preserve a constant volume when the temperature is changed? Coefficient of linear expansion of iron  $12 \times 10^{-6}$  per degree C. Coefficient of cubical expansion of glass  $25 \times 10^{-6}$  per degree C.

13. Explain a method for the determination of the manner in which the density of a solid varies with temperature.

At  $0^{\circ}\text{C}$  the density of solid A is  $7.3 \text{ gm. cm.}^{-3}$ , of solid B  $7.4 \text{ gm. cm.}^{-3}$ . Their coefficients of linear expansion are  $0.000011$  and  $0.000025$  per degree C. respectively. At what temperature will their densities be equal?

14. Explain why the time given by a clock tends to vary with temperature. Describe and explain some devices used to overcome the difficulties associated with this variation.

15. Make a careful drawing, with brief explanation, of apparatus suitable for measuring the real coefficient of expansion of mercury. Prove the formula used for deducing the coefficient.

16. Give the theory of the weight thermometer, and explain how you would use it to measure the coefficient of expansion of mercury.

17. Draw a diagram illustrating the apparatus used for the determination of the absolute coefficient of expansion of mercury. Describe the method briefly and show how the calculation is made.

A glass vessel full of mercury at  $15^{\circ}\text{C}$  contains 400 gm. Determine the additional amount required to fill it at  $0^{\circ}\text{C}$ . [Coeff. of expansion of mercury =  $0.000181$ , coeff. for glass =  $0.000024$ .]

18. A piece of quartz is weighed in ice-cold water and is found to weigh  $W_0$  gm. It is weighed again in water at temperature  $t$  and found to weigh  $W_t$  gm. If the weight of the quartz in air is  $W$  gm., find an expression for the coefficient of expansion of water between  $0^{\circ}$  and  $t^{\circ}$ , assuming that the thermal expansion of quartz is negligible. How is the expression modified if the quartz is replaced by a piece of glass of coefficient of expansion  $\beta$ ?

19. Establish a relation between the real and apparent expansion coefficients of a liquid.

Explain fully how the real expansion coefficient of a liquid may be found by weighing a solid of known expansion coefficient in it at different temperatures.

20. Enunciate Boyle's law.

A barometer with a little air in the space above the mercury reads 75 cm. when the atmospheric pressure is 76 cm. of mercury, and 74.2 cm. when the atmospheric pressure is 75 cm. What will it read when the atmospheric pressure is 77 cm.?

21. Enunciate Boyle's law. Explain how you would illustrate the law by means of the usual apparatus if a barometer is not available.

22. State Boyle's law and Charles' law, and derive from them the relation  $p\nu = RT$ .

Calculate the value of  $R$  in the case of 1 grm. of oxygen, whose density is 0.00143 grm. per c.c. at  $0^{\circ}\text{C}$ . and 76 cm. of mercury pressure. State the units in which  $R$  is expressed. [Density of mercury, 13.6 grm. per c.c.;  $g = 981$  cm. per sec.<sup>2</sup>.]

23. Give a short account of the experiments which have been made on the relation between the pressure, volume, and temperature of gases, and of the results obtained.

Three vessels A, B, and C, of volumes 1, 2, and 3 litres respectively, each contain air. The pressures and temperatures of the air in the three vessels are 70 cm. and  $70^{\circ}\text{C}$ ., 75 cm. and  $27^{\circ}\text{C}$ ., and 72.5 cm. and  $7^{\circ}\text{C}$ . respectively. If the three vessels are connected and the final temperature is  $0^{\circ}\text{C}$ ., what is the final pressure?

24. How is temperature defined by means of the constant pressure gas thermometer? Show that this definition combined with Boyle's law for gases leads to the equation  $p\nu = RT$ .

Describe how the value of  $T$  corresponding to the temperature of melting ice could be determined by experiment.

25. What is meant by a centigrade scale of temperature? How is a centigrade temperature defined on (a) a constant volume gas thermometer, (b) a platinum resistance thermometer?

Describe a platinum resistance thermometer and explain how it may be used to measure temperature.

#### *Calorimetry. Chapter VII*

26. Define unit of heat, thermal capacity, specific heat. Discuss carefully the question whether specific heat does, or does not, possess dimensions in mass, length, and time.

27. Describe how you would determine the specific heat of brine, indicating carefully the precautions you would take to minimise experimental errors.

28. Draw a temperature-time diagram showing the change of temperature immediately before, during, and just after the insertion of the hot solid into the calorimeter on the determination of specific heat by the method of mixtures. Explain how the correction for heat losses may be obtained by means of the graph.

A piece of copper at  $100^{\circ}\text{C}$ . is dropped into a calorimeter containing ice-cold water, and the final temperature of the mixture is  $10^{\circ}\text{C}$ . An equal mass of iron is heated and dropped into the calorimeter containing again the same amount of water and with the attainment of the same final temperature. The specific heats being 0.093 and 0.113 respectively, find the initial temperature of the iron.

29. Describe a good method for the determination of the specific heat of a liquid such as water where a large quantity is available.

#### *Change of State. Chapters VIII. and IX*

30. Describe experiments to show how the freezing point of water is affected (a) by pressure, (b) by the presence of dissolved substances in the water. Discuss any consequences or practical applications of these facts.

31. 20 grm. of ice are placed in a thin metal tube and cooled to  $-15^{\circ}\text{C}$ . by placing in a freezing mixture. The tube containing the ice is then quickly transferred to a calorimeter containing 250 grm. of water at  $20^{\circ}\text{C}$ . and the

resulting temperature is  $12^{\circ}\text{C}$ . A second experiment is performed using 30 grm. of ice cooled to  $-10^{\circ}\text{C}$ . and transferring to 300 grm. of water at  $25^{\circ}\text{C}$ ., the resulting temperature being  $15^{\circ}\text{C}$ . The water equivalent of the calorimeter is 6 grm. and of the tube 2 grm. Calculate (a) the latent heat of fusion of ice, (b) its specific heat.

32. Describe how you would demonstrate that water has its maximum density at  $4^{\circ}\text{C}$ ., and draw a graph showing the general character of the variation of density with temperature as ice at about  $-20^{\circ}\text{C}$ . is converted to water at about  $10^{\circ}\text{C}$ .

How is the change of density at the melting point applied in the determination of specific heat?

33. Write a short account of latent heat calorimetry.

A block of copper (specific heat 0.092), at a temperature of  $40^{\circ}\text{C}$ ., is placed on a large block of ice at  $0^{\circ}\text{C}$ . Assuming that all the heat from the copper passes into the ice, find the fraction of the total volume of the copper that is embedded in the ice when equilibrium is attained. [The densities of copper and ice are 8.6 and 0.92 grm. per c.c. respectively; the latent heat of fusion of ice is 80 calories per grm.]

34. Make a diagram of Bunsen's ice calorimeter and explain its use in determining the specific heat of a liquid.

In a calorimeter of this type it is found that the mercury creeps along the capillary tube at the rate of 1 cm. per 5 min. If this is due to the entrance of heat through the test-tube part of the apparatus, determine the rate of supply of heat. The diameter of the capillary tube is 1 mm., the density of ice 0.92 grm. per c.c., and the latent heat of fusion 80 calories per grm.

35. How would you determine the latent heat of vaporisation of alcohol?

36. How would you determine with precision the melting point and the boiling point of substances available only in small quantities?

37. Give an account of the effect of changes of pressure on (a) the boiling point of a liquid, (b) the melting point of a solid. How would you investigate experimentally the effect of changes of pressure on the boiling point of water?

38. Describe a method for the determination of the latent heat of vaporisation of alcohol.

150 grm. of alcohol at a temperature of  $63.3^{\circ}\text{C}$ . are contained in a copper vessel of mass 200 grm. How much water at  $98.3^{\circ}\text{C}$ . would be required to be poured into the vessel in order just to cause the alcohol to evaporate, if the process be assumed to consist in first raising the alcohol to its boiling point and then boiling it? Make use of the following data: Sp. heat of copper 0.1, boiling point of alcohol  $78.3^{\circ}\text{C}$ ., latent heat of alcohol 205 cal. per grm., sp. heat of alcohol 0.58.

39. Describe Joly's steam calorimeter and explain how it may be used to determine the latent heat of steam.

40. How would you measure the specific heat of a gas at constant volume? The specific heat of hydrogen at constant pressure is  $3.41 \text{ cal. grm.}^{-1} (\text{degree C.})^{-1}$ . Calculate its specific heat at constant volume, assuming it to have the properties of a perfect gas.

41. Describe two methods of finding specific heats, one depending on the change in volume when ice melts, the other on the heat given out when steam condenses.

Deduce an expression for the difference between the specific heats of a perfect gas at constant pressure and constant volume.

42. Explain what is meant by saying that the latent heat of water is 80 cal. per grm. and the latent heat of steam 540 cal. per grm.? Express these quantities in pound Centigrade units and in British thermal units.

10 lb. of steam at  $100^{\circ}\text{C}$ . are blown into a tank containing a mixture of ice and water at  $0^{\circ}\text{C}$ . and weighing 120 lb. If the temperature rises to  $15^{\circ}\text{C}$ ., determine the weight of ice initially in the mixture. The thermal capacity of the tank may be neglected.

*Vapours and Hygrometry. Chapters X. and XI*

43. What do you understand by the term saturation vapour pressure?

How would you measure the saturation vapour pressure of water at different temperatures over the range  $50^{\circ}\text{C}$ . to  $100^{\circ}\text{C}$ .?

44. How would you measure the saturation pressure of aqueous vapour over the range  $10^{\circ}\text{C}$ .- $50^{\circ}\text{C}$ .?

A litre of air is collected in a cylindrical jar over water at  $15^{\circ}\text{C}$ ., the barometer reading 750 mm., and the level of the water in the jar being 13.6 cm. above that of the external water. Calculate the volume of dry air at standard temperature and pressure, given that the maximum pressure of aqueous vapour at  $15^{\circ}\text{C}$ . is 12.7 mm. of mercury.

45. Give an account of the laws which govern the behaviour of saturated vapours, and describe experiments illustrating the laws.

A litre of gas is collected over water at a total pressure of 772 mm. of mercury. The gas is then expanded to 1400 c.c., but is kept saturated with water vapour at the same temperature, the saturation vapour pressure being 12 mm. of mercury. Find the total pressure after expansion.

46. Describe the principal laws associated with the change of state from liquid to gas in the case of water.

It is found that in order to halve the volume of a quantity of air confined over mercury on which some water is standing the pressure has to be raised from 60 to 105 mm. of mercury, the temperature remaining constant. What conclusions can you draw?

47. State and explain Dalton's law of partial pressures.

A closed vessel contains water and air. At  $17^{\circ}\text{C}$ . and  $89.5^{\circ}\text{C}$ . the pressures in mm. of mercury are 774.5 mm. and 1470 mm. respectively. If the vapour pressure of water at  $17^{\circ}\text{C}$ . is 14.5 mm. and some of the water remains as a liquid at  $89.5^{\circ}\text{C}$ ., find the vapour pressure of water at the latter temperature.

48. Explain the law of partial pressures in its application to mixtures of gases.

In an apparatus for the verification of Boyle's law some liquid is introduced above the mercury into the enclosed gas. The temperature of the mixture remains constant and some liquid is always present. What happens as the volume is varied by raising or lowering the mercury column? If the reciprocal of the volume be plotted against the total pressure of the mixture, what graph is obtained? How may the vapour pressure of the liquid be obtained from the graph?

49. What is the difference between the pressure-volume relation for a gas and for a saturated vapour, the temperature being constant? Describe experiments illustrating your answer.

A gas of volume 500 c.c. is saturated with vapour at a temperature at which the saturation pressure is 15 mm. of mercury. The total pressure is 795 mm. and with constant temperature the volume is halved. Find the resulting total pressure.



50. Distinguish between an unsaturated and a saturated vapour. Describe fully how you would determine the pressure of the water vapour in the atmosphere. What further information is necessary in order to estimate the humidity of the atmosphere?

51. Write a short essay on hygrometry.

52. Explain the terms saturation vapour pressure, relative humidity.

A cubic metre of air at  $20^{\circ}\text{C}$ . having a relative humidity of 60 per cent. is compressed isothermally until its volume is 10 litres. Find the mass of water condensed. (The saturation pressure of water vapour at  $20^{\circ}\text{C}$ . is 17.5 mm.; the density of air at S.T.P. is  $0.00129\text{ gm. cm.}^{-3}$ , the density of water vapour is  $\frac{1}{8}$  that of air at the same temperature and pressure.)

53. Define relative humidity and dew point.

Find the weight of a cubic metre of air saturated with aqueous vapour at  $20^{\circ}\text{C}$ ., given that the density of dry air at N.T.P. is  $0.001293\text{ gm./c.c.}$ , that the saturation pressure of aqueous vapour at  $20^{\circ}\text{C}$ . is 17.4 mm. of mercury, and that the density of aqueous vapour is five-eighths that of dry air at the same temperature and pressure.

54. What apparatus would you use in order to determine the dew point accurately in a laboratory? Describe the method of use and how the relative humidity may be obtained.

Describe the principle of the wet and dry bulb hygrometer and state under what conditions it is used.

55. Define dew point and relative humidity.

Explain how the relative humidity may be found by the use of an absorption hygrometer.

A cubic metre of air at  $20^{\circ}\text{C}$ . when saturated contains 17.12 gm. of water vapour. If water vapour is  $\frac{1}{8}$  as heavy as air and air weighs 1.293 gm. per litre at  $0^{\circ}\text{C}$ . and 76 cm. of mercury pressure, calculate the saturation vapour pressure of water at  $20^{\circ}\text{C}$ .

56. Define relative humidity, and explain how it may be determined.

Calculate the total mass of the moist air in a room 12 m.  $\times$  10 m.  $\times$  8 m. when the temperature is  $15^{\circ}\text{C}$ ., the barometric height 75.5 cm., and the relative humidity 60 per cent. The density of air at standard temperature and pressure is 1.29 gm. per litre, the density of water vapour is  $\frac{1}{8}$  that of air at the same temperature and pressure, and the maximum vapour pressure of water at  $15^{\circ}\text{C}$ . is 12.7 mm.

#### *Mechanical Equivalent of Heat, Properties and Liquefaction of Gases. Chapters XII. to XIV*

57. Write a short essay on the principle of the conservation of energy.

58. Describe and explain a mechanical method for the determination of Joule's equivalent. (Do not describe Joule's original method.)

The water from a slow-moving stream falls vertically through 100 ft. Calculate approximately the amount by which the temperature at the bottom of the fall exceeds that at the top.

59. Explain what is meant by saying that 778 ft.-lb. of work are equivalent to 1 British Thermal Unit.

Describe a mechanical method for determining this relation, stating the precautions to be taken to ensure an accurate result.

60. Describe an experiment which shows that there is a quantitative relation between heat and mechanical or electrical energy.

A body falling from a great height attains a limiting velocity on account of friction and thereafter falls at uniform speed. If the limiting velocity be 80 km. per hr. in the case of a body weighing 1 kgm., find the rate of development of heat in calories per sec.

61. Describe the continuous flow method of determining the mechanical equivalent of heat and point out the advantages of the method.

A bullet moving horizontally strikes a target and comes to rest. Assuming that all the heat remains in the bullet, find its velocity if it just melts completely on striking the target. The initial temperature of the bullet is  $15^{\circ}\text{C}$ ., its melting point  $515^{\circ}\text{C}$ ., its specific heat 0.04, and its latent heat of fusion 40 calories per grm. The mechanical equivalent of heat may be taken as  $4.2 \times 10^7$  ergs per calorie.

62. Describe a friction-brake method for the determination of the mechanical equivalent of heat. Show how the result is calculated from the observations and state the precautions necessary to ensure an accurate result.

63. Explain why there is a difference between the specific heat of a gas at constant pressure and at constant volume. Deduce an expression for the difference in the case of a perfect gas.

Describe a method of measuring the specific heat of a gas at constant volume.

\* 64. Deduce an expression for the work done when a gas expands at constant pressure  $p$  so that its volume increases by an amount  $\delta v$ .

Show how this formula may be used in the determination of the difference of the specific heats at constant pressure and at constant volume in the case of a perfect gas. Assuming that air is approximately a perfect gas, find the difference in this case given that the density at N.T.P. is 1.29 grm. per litre and that 1 atmosphere is equal to a pressure of  $10^6$  dynes per sq. cm.

65. Explain (a) isothermal, (b) adiabatic, expansion, and give the corresponding relations between pressure and volume for a perfect gas.

Air, initially at a pressure of 10 atmospheres, is allowed to escape slowly from a cylinder of volume 0.50 cub. ft., the temperature remaining constant at  $0^{\circ}\text{C}$ . The volume of the escaped air at  $17^{\circ}\text{C}$ . and atmospheric pressure is 2.9 cub. ft. Calculate the final pressure in the cylinder.

66. Contrast the variation of pressure with volume in the following cases: (a) an isothermal change in a perfect gas, (b) an adiabatic change in a perfect gas, and (c) an isothermal change in a mixture of a perfect gas and a saturated vapour.

A horizontal tube closed at one end contains a mixture of air and saturated water vapour at  $30^{\circ}\text{C}$ . The length of the gas column is 40 cm. and is shut off from the outside by a pellet of mercury 4 cm. long. Find the length of the gas column when the tube is vertical with the closed end downwards, the temperature remaining the same. The atmospheric pressure is 76 cm. of mercury and the saturation pressure of the vapour at  $30^{\circ}\text{C}$ . is 3.2 cm. of mercury.

67. Describe a method of finding (a) the specific heat of a gas at constant volume, (b) the ratio of the specific heats of a gas at constant pressure and constant volume. Explain how the results would be deduced in each case.

Explain briefly why a knowledge of the ratio of the specific heats is important.

68. Describe how the specific heat of a gas at constant volume may be determined.

Discuss the importance of a knowledge of (a) the ratio of, (b) the difference between, the two principal specific heats of a gas.

69. Give an account of the experiments which have been made on the relation between the pressure, volume and temperature of a gas, and of the results obtained. How have the departures from the simple laws been explained?

70. Give an account of Andrew's experiment on the pressure-volume relation in the case of carbon dioxide during isothermal changes.

Explain the significance of the experiment for the process of condensation of gases. Draw curves to explain the results obtained.

71. Give an account of the pressure-volume relations of hydrogen and nitrogen at constant temperature.

A long narrow tube of uniform bore contains dry air imprisoned by a pellet of mercury 15 cm. long. When the tube is held vertically with the closed end uppermost, the air column is 30 cm. long, while with the closed end downwards it is 20 cm. long. In this latter position the open end of the tube is connected to a high pressure gas supply, and now the length of the air column is 19 cm. Find the pressure of the gas supply.

72. Draw curves showing how gases deviate from Boyle's law at high pressures. How have these deviations been explained? Describe experiments that have shown the existence of a critical temperature for gases.

73. Describe an experiment which shows the existence of a critical pressure in the case of gases. Illustrate the results obtained by means of a graph and explain their importance in the liquefaction of gases.

Describe briefly a method for the liquefaction of such a gas as oxygen.

74. Write an essay on the liquefaction of gases.

75. Describe a method of producing liquid air on a large scale and mention the principles involved.

How must the method be modified if hydrogen is to be liquefied?

#### *Convection, Conduction, and Radiation. Chapters XV. to XVII*

76. Write an essay, giving as many illustrative examples as possible, on the convective transference of heat energy. Give carefully drawn diagrams where necessary.

77. Define thermal conductivity and temperature gradient.

A circular glass plate, 2 mm. thick, is sandwiched between two aluminium discs of the same diameter as the glass but each 2 cm. thick. The exposed face of one aluminium disc is maintained at  $100^{\circ}\text{C}$ . and that of the other at  $0^{\circ}\text{C}$ . Assuming no lateral loss of heat, determine the temperatures of the faces of the glass plate and how much heat flows through an area of 1 sq. cm. of the plate in one minute. [Thermal conductivity of aluminium, 0.50; of glass, 0.0025; in c.g.s. Centigrade units.]

78. What is meant by the coefficient of thermal conductivity of a substance? If the numerical value of the coefficient for a substance is 0.2 when the units of mass, length, and temperature are 1 grm., 1 cm., and  $1^{\circ}\text{C}$ . respectively, what will be its numerical value if these units are changed to 1 lb., 1 ft., and  $1^{\circ}\text{F}$ . respectively?

Describe a method of measuring the coefficient of thermal conductivity of a metal in the form of a bar.

79. Describe methods for the measurement of the thermal conductivity of a metal bar and of a piece of cardboard.

80. Define the coefficient of thermal conductivity of a substance. Why are different methods necessary for the determination of the coefficient for different types of substance?

Describe (a) a method of comparing the coefficients of thermal conductivity of two good conductors, (b) a method of determining absolutely the coefficient of thermal conductivity of a good conductor.

81. How would you compare the thermal conductivities of two metals?

A lagged metal rod of length 50 cm. and diameter 2 cm. has one end maintained at  $100^{\circ}\text{C.}$ , while the other end terminates in a vessel containing ice. It is found that 23.5 grm. of ice are melted in 10 min. Calculate the conductivity of the metal.

82. Define thermal conductivity, and write the fundamental equation in a form which will exhibit its analogy to the corresponding expression for Ohm's law.

A sheet of metal 2 mm. thick is placed in contact with a sheet of glass 4 mm. thick. The outer surfaces of the metal and the glass are at temperatures of  $100^{\circ}\text{C.}$  and  $0^{\circ}\text{C.}$  respectively. If the thermal conductivities in c.g.s. units of the metal and the glass are 0.075 and 0.002 respectively, calculate the temperature of the interface.

83. Define thermal conductivity.

Water passes through a glass tube 30 cm. long at the rate of 165 cm.<sup>3</sup> per min. It enters the tube at  $20^{\circ}\text{C.}$  and leaves at  $40^{\circ}\text{C.}$ , the outside of the tube being maintained at  $100^{\circ}\text{C.}$  If the internal and external radii of the tube are 6 mm. and 8 mm. respectively, determine the thermal conductivity of the glass.

Draw a diagram showing the arrangement of the apparatus required for the performance of the experiment indicated in this problem.

84. How would you determine the conductivity of glass in the form of a circular disc of about 10 cm. diameter and of thickness 3 mm.?

The glass windows of a room have a total area of 8 sq. m. and are 3 mm. thick. The outside temperature is  $0^{\circ}\text{C.}$  What rate of expenditure of energy expressed in horse-power units is required to maintain a temperature of  $20^{\circ}\text{C.}$  in the room, if the only loss of heat is through the windows? 1 calorie =  $4.2 \times 10^7$  ergs.  $10^7$  ergs per sec. = 1 watt. 746 watts = 1 H.-P. Thermal conductivity of glass =  $17 \times 10^{-4}$  cal. per cm. per sec. per degree C.

85. Describe by means of graphs the temperature fall along a metal rod heated at one end and cooled at the other (a) when radiation is prevented, and (b) when radiation takes place.

Explain the essential differences in experiments for the measurement of the thermal conductivity in the cases of good and bad conductors, giving an example in illustration.

86. Upon what conditions does the rate of radiation from a body depend?

Discuss the relation between the radiating, absorbing, and reflecting powers of a surface, illustrating your statements by examples.

87. Explain in detail how it can be shown that heat radiation (a) obeys the law of inverse square, and (b) is reflected and refracted in the same way as light.

Give some other points of resemblance between heat and light radiation.

88. Describe the thermopile and explain how you would use it to compare the intensities of the radiation at various distances from a small source. What results would you expect?

89. Describe in detail the apparatus used and the method employed in investigating the emissive power of a surface.

Discuss in a general way the statement that "a good absorber is a good radiator."

90. Describe (a) a thermocouple and (b) a thermopile.

How would you compare the radiating powers of bright and blackened metal surfaces?

Describe an experiment to show that the radiating and absorbing powers of surfaces are directly proportional to one another.

91. A hot body is allowed to cool through a definite range of excess temperature in an enclosure containing air at atmospheric pressure. The experiment is repeated several times with lower and lower air pressures in the enclosure. How does the rate of cooling alter?

How will the rate of cooling vary with the temperature of the body and of the enclosure (a) at atmospheric pressure, (b) at very low pressures?

92. State Newton's law of cooling. In what circumstances is it true? Describe how you would verify it in some particular case.

93. Describe how you would measure by the method of cooling the mean specific heat of a liquid such as turpentine over the range  $40^{\circ}$ - $50^{\circ}$  C. Discuss the necessary precautions and corrections.

94. State Newton's Law of Cooling. What is the nature of the losses or gains of heat included in this law?

A heating coil is immersed in water in a metal container and it is found that a current of 5 amperes supplied at 10 volts to the coil maintains a constant temperature of  $30^{\circ}$  C. when the surroundings are at  $20^{\circ}$  C. Find the constant in the cooling equation.

When the mass of the container is 200 grm. and the weight of the water also 200 grm. it is found that, with the coil removed, the vessel falls from  $27^{\circ}$  to  $23^{\circ}$  in 168 sec., the surroundings being at  $20^{\circ}$  C. Find the specific heat of the metal of which the container is made.

95. State Newton's law of cooling and Stefan's law of radiation.

A black body is placed in an evacuated enclosure whose walls are blackened and kept at  $27^{\circ}$  C. Compare the net amounts of heat gained or lost by the body (a) when its temperature is  $127^{\circ}$  C. and (b) when its temperature is  $-73^{\circ}$  C.

96. State Stefan's law of radiation. Describe a type of pyrometer based on this law suitable for measuring furnace temperatures in the neighbourhood of  $1000^{\circ}$  C.

### *Kinetic Theory of Gases.* Chapter XVIII

97. Give a brief account of the kinetic theory of gases, and show that on certain assumptions the theory leads to Boyle's law.

98. How is the pressure of a gas explained on the kinetic theory? Deduce an expression for the pressure of a gas in terms of its density and the root mean square velocity of its molecules. Calculate the root mean square velocity of the molecules of hydrogen at  $0^{\circ}$  C.

99. Write an account of Van der Waals' equation. Show that this equation is consistent with the observed deviations from Boyle's law.

100. How does elementary kinetic theory account for the pressure-volume relation of a gas such as hydrogen.

At what centigrade temperature will oxygen molecules have the same mean velocity as that of the molecules of hydrogen gas at  $-100^{\circ}$  C.?

101. Describe a method of measuring the latent heat of vaporisation of water.

Find the difference between the internal energy of 1 gram. of water and 1 gram. of steam at  $100^{\circ}\text{C}$ ., given that the volume of 1 gram. of steam at  $100^{\circ}\text{C}$ . and normal pressure is 1501 c.c. Normal pressure may be taken as  $10^6$  dynes per sq. cm.; the mechanical equivalent of heat as  $4.2 \times 10^7$  ergs per calorie.

102. Deduce an expression for the work done when a gas expands.

1 gram. molecule of oxygen at 76 cm. pressure and  $27^{\circ}\text{C}$ . expands until its volume is doubled (a) at constant pressure, (b) isothermally, (c) adiabatically. Find the work done in the expansion in each case. The ratio of the specific heats of oxygen at constant pressure and constant volume may be taken as 1.4.

# TABLES OF PHYSICAL CONSTANTS

## I

### SOME IMPORTANT TEMPERATURES

The sun .. ..	5900° C.	Healthy human body ..	36·8° C. (98·4° F.)
The electric arc ..	3500° C.	Mean temperature of sea	17° C. (62° F.)
Bessemer furnace ..	2230° C.	Mixture of ice and salt..	- 17·7° C. (0° F.)
Oxy-hydrogen flame ..	2200° C.	Lowest natural tempera- ture recorded.. ..	- 69° C.
White heat .. ..	1500° C.	Lowest temperature reached .. ..	- 272·3° C.
Orange-red heat ..	1100° C.	Absolute zero .. ..	- 273·1° C. (- 459° F.)
Cherry-red heat ..	900° C.		
Dull-red heat .. ..	700° C.		
Ignition of coal ..	400° C.		
Highest shade temperature recorded .. ..	53° C. (127·4° F.)		

## II

### COEFFICIENTS OF LINEAR EXPANSION OF SOLIDS

*The values are mean coefficients between 0° C. and 100° C.*

Invar (nickel steel) ..	0·0000009	Brass .. ..	0·000019
Quartz (parallel to axis)	0·0000075	Silver .. ..	0·000019
Glass (soft) .. ..	0·0000086	Tin .. ..	0·000021
Platinum .. ..	0·0000089	Lead .. ..	0·000028
Cast iron .. ..	0·000011	Zinc .. ..	0·000029
Steel .. ..	0·000012	Oak .. ..	0·00005
Quartz (perpendicular to axis) .. ..	0·0000137	Ice (- 10° C. to 0° C.)	0·000051
Copper .. ..	0·000017	Sulphur .. ..	0·00007

## III

### COEFFICIENTS OF ABSOLUTE EXPANSION OF LIQUIDS

*The values are mean coefficients between 0° C. and 40° C.*

Mercury .. ..	0·000181	Turpentine .. ..	0·00094
Water .. ..	0·000193	Ethyl alcohol .. ..	0·00110
Glycerin .. ..	0·00053	Carbon bisulphide ..	0·00121
Aniline .. ..	0·00085	Chloroform .. ..	0·00126
Paraffin oil .. ..	0·00090	Ether .. ..	0·00163

## IV

THE DENSITY ( $\delta$ ) OF WATER, AND THE VOLUME ( $v$ ) OF 1 GRM.  
OF WATER AT VARIOUS TEMPERATURES ( $^{\circ}$  C.)

$t$			$\delta$			$v$
0° (ice)	..	..	0.9169	..	..	1.0906
0° (water)	..	..	0.999874	..	..	1.000127
1	..	..	0.999930	..	..	1.000071
2	..	..	0.999970	..	..	1.000030
3	..	..	0.999993	..	..	1.000007
4	..	..	1.000000	..	..	1.000000
5	..	..	0.999992	..	..	1.000008
6	..	..	0.999970	..	..	1.000030
7	..	..	0.999932	..	..	1.000068
8	..	..	0.999881	..	..	1.000119
9	..	..	0.999815	..	..	1.000185
10	..	..	0.999736	..	..	1.000265
12	..	..	0.999537	..	..	1.000464
14	..	..	0.999287	..	..	1.000714
16	..	..	0.998988	..	..	1.001013
18	..	..	0.998642	..	..	1.001360
20	..	..	0.998252	..	..	1.001751
25	..	..	0.997098	..	..	1.002911
30	..	..	0.995705	..	..	1.004314
35	..	..	0.994098	..	..	1.005936
40	..	..	0.99233	..	..	1.00733
45	..	..	0.99035	..	..	1.00974
50	..	..	0.98813	..	..	1.01201
55	..	..	0.98579	..	..	1.01442
60	..	..	0.98331	..	..	1.01697
65	..	..	0.98067	..	..	1.01971
70	..	..	0.97790	..	..	1.02260
75	..	..	0.97495	..	..	1.02569
80	..	..	0.97191	..	..	1.02890
85	..	..	0.96876	..	..	1.03224
90	..	..	0.96550	..	..	1.03574
95	..	..	0.96212	..	..	1.03938
100 (water)	..	..	0.95863	..	..	1.04315
100 (steam)	..	..	0.000598	..	..	1672.5

## V

GAS COEFFICIENTS BETWEEN 0° C. AND 100° C. (REGNAULT)

	AT CONSTANT VOLUME (INITIAL PRESSURE ATMOSPHERIC)	AT CONSTANT PRESSURE (ATMOSPHERIC)
Air .. ..	0.0036650	0.0036706
Hydrogen .. ..	0.0036678	0.0036613
Oxygen .. ..	0.0036743	—
Nitrogen .. ..	0.0036682	0.0036709
Carbon dioxide ..	0.0036856	0.0037099
Sulphur dioxide ..	0.0038450	0.0039028



VI  
SPECIFIC HEATS

Solids				Gases (at constant pressure)			
Lead ..	..	..	0.031	Carbon dioxide ..	..	0.201	
Tin ..	..	..	0.055	Air ..	..	0.242	
Brass ..	..	..	0.094	Oxygen ..	..	0.242	
Copper ..	..	..	0.095	Nitrogen ..	..	0.235	
Zinc ..	..	..	0.094	Steam ..	..	0.488	
Iron ..	..	..	0.114	Hydrogen ..	..	3.402	
Sulphur ..	..	..	0.178	Gases (at constant volume)			
Glass (thermometer) ..	..	..	0.198	Carbon dioxide ..	..	0.165	
Aluminium ..	..	..	0.214	Air ..	..	0.172	
Ice (— 78° C. to 0° C.) ..	..	..	0.474	Oxygen ..	..	0.173	
Liquids				Nitrogen ..	..	0.175	
Mercury ..	..	..	0.033	Steam ..	..	0.340	
Turpentine ..	..	..	0.426	Hydrogen ..	..	2.402	
Glycerin ..	..	..	0.555				
Alcohol ..	..	..	0.620				

VII  
ATOMIC HEATS

	ATOMIC WEIGHT	SPECIFIC HEAT	ATOMIC HEAT
Aluminium ..	27	0.214	5.8
Sulphur ..	32	0.178	5.7
Iron ..	56	0.114	6.4
Copper ..	63	0.095	6.0
Zinc ..	65	0.094	6.0
Tin ..	118	0.055	6.5
Iodine ..	126	0.054	6.8
Gold ..	197	0.032	6.4
Lead ..	206	0.031	6.4
Uranium ..	239	0.028	6.7

VIII  
MELTING POINTS

Platinum ..	1756° C.	Potassium sulphate ..	1067° C.
Iron (pure) ..	1530° C.	Borax ..	1000° C.
Copper ..	1083° C.	Common salt ..	801° C.
Gold ..	1062° C.	Anthracene ..	216° C.
Silver ..	960° C.	Tartaric acid ..	170° C.
Aluminium ..	657° C.	Cane sugar ..	189° C.
Zinc ..	418° C.	Sulphur ..	115° C.
Lead ..	327° C.	Naphthalene ..	80° C.
Cadmium ..	321° C.	White wax ..	68° C.
Bismuth ..	269° C.	Paraffin wax ..	54° C.
Tin ..	232° C.	Phosphorus ..	44.1° C.
Sodium ..	97.6° C.	Benzene ..	5.4° C.
Mercury ..	— 38.8° C.	Ice ..	0° C.
Oxygen ..	— 219° C.	Aniline ..	— 6.4° C.
Hydrogen ..	— 259° C.	Alcohol ..	— 115° C.
Helium ..	— 272° C.	Ether ..	— 123° C.

## IX

## LATENT HEATS OF FUSION

Ice .. ..	79·8	Silver .. ..	22
Sodium nitrate .. ..	63	Tin .. ..	14·6
Potassium nitrate .. ..	47	Sulphur .. ..	9·4
Paraffin wax .. ..	35	Lead .. ..	5·5
Zinc .. ..	26·6	Mercury .. ..	3

## X

## BOILING POINTS

*At the pressure equal to that of 760 mm. of mercury at 0° C.*

Air (liquid) .. ..	- 191° C.	Water (distilled) .. ..	100·0° C.
Carbon dioxide (liquid) .. ..	- 78·2° C.	Turpentine (spirits) .. ..	130·3° C.
Ammonia (liquid) .. ..	- 33·5° C.	Turpentine (oil) .. ..	159·1° C.
Sulphur dioxide (liquid) .. ..	- 10·8° C.	Aniline .. ..	183·9° C.
Ether .. ..	34·6° C.	Naphthalene .. ..	218° C.
Chloroform .. ..	61·2° C.	Sulphuric acid .. ..	325° C.
Alcohol .. ..	78·3° C.	Mercury .. ..	356·7° C.
Benzene .. ..	80·2° C.	Sulphur .. ..	444·5° C.

## XI

## LATENT HEATS OF VAPORISATION

*At boiling point under a pressure of 760 mm. of mercury at 0° C.*

Water .. ..	540	Turpentine (oil) .. ..	74
Sulphur .. ..	362	Mercury .. ..	68
Alcohol .. ..	202	Oxygen (liquid) .. ..	58
Ether .. ..	90	Air (liquid) .. ..	55

## XII

MAXIMUM PRESSURE OF AQUEOUS VAPOUR BETWEEN 85° C.  
AND 102° C.

*Pressures are in mm. of mercury at 0° C.*

<i>t</i>	<i>p</i>	<i>t</i>	<i>p</i>
85° C.	433·5	94° C.	611·0
86° C.	450·8	95° C.	634·0
87° C.	468·6	96° C.	657·7
88° C.	487·1	97° C.	682·1
89° C.	506·1	98° C.	707·3
90° C.	525·8	99° C.	733·3
91° C.	546·1	100° C.	760·0
92° C.	567·1	101° C.	787·5
93° C.	588·7	102° C.	815·9

## XIII

MAXIMUM PRESSURE OF AQUEOUS VAPOUR BETWEEN  
— 10° C. AND 200° C.

*Pressures are in mm. of mercury at 0° C.*

<i>t</i>	<i>p</i>	<i>t</i>	<i>p</i>
— 10° C.	2·1	70° C.	233·5
— 5° C.	3·1	80° C.	355·1
0° C.	4·6	90° C.	525·8
5° C.	6·5	95° C.	634·0
10° C.	9·2	100° C.	760·0
15° C.	12·8		(1 atmosphere)
20° C.	17·5	110° C.	1074·5
30° C.	31·8	120° C.	1488·9
40° C.	55·3	150° C.	3568·7
50° C.	92·5		(4·7 atmospheres)
60° C.	149·2	200° C.	11647·0
			(15·4 atmospheres)

## XIV

PRESSURE OF MERCURY VAPOUR AT DIFFERENT TEMPERATURES

*Pressures are in mm. of mercury at 0° C.*

<i>t</i>	<i>p</i>	<i>t</i>	<i>p</i>
0° C.	0·0002	200° C.	17·81
50° C.	0·0122	300° C.	248·6
100° C.	0·276	356·7° C.	760·0

## XV

BOILING POINT OF WATER AT PRESSURES BETWEEN  
740 MM. AND 780 MM.

*Pressures are in mm. of mercury at 0° C.*

<i>p</i>	<i>t</i> ° C.	<i>p</i>	<i>t</i> ° C.	<i>p</i>	<i>t</i> ° C.	<i>p</i>	<i>t</i> ° C.
740	99·26	750	99·63	760	100·00	770	100·36
741	99·30	751	99·67	761	100·04	771	100·40
742	99·33	752	99·71	762	100·07	772	100·44
743	99·37	753	99·74	763	100·11	773	100·47
744	99·41	754	99·78	764	100·15	774	100·51
745	99·44	755	99·82	765	100·18	775	100·55
746	99·48	756	99·85	766	100·22	776	100·58
747	99·52	757	99·89	767	100·26	777	100·62
748	99·56	758	99·93	768	100·29	778	100·65
749	99·59	759	99·96	769	100·33	779	100·69
750	99·63	760	100·00	770	100·36	780	100·73

## XVI

PRESSURE OF AQUEOUS VAPOUR ( $f$ ) IN MM. OF MERCURY,  
AND MASS OF WATER ( $m$ ) IN GRM. PER CUB. M. OF AIR WITH  
DEW-POINT ( $t^{\circ}$  C.)

$t$	$f$	$m$	$t$	$f$	$m$	$t$	$f$	$m$	$t$	$f$	$m$
-10	2.0	2.1	0	4.6	4.9	10	9.2	9.4	20	17.5	17.2
-9	2.2	2.4	1	4.9	5.2	11	9.8	10.0	21	18.6	18.2
-8	2.4	2.7	2	5.3	5.6	12	10.5	10.6	22	19.8	19.3
-7	2.6	3.0	3	5.7	6.0	13	11.2	11.3	23	21.0	20.4
-6	2.8	3.2	4	6.1	6.4	14	12.0	12.0	24	22.3	21.5
-5	3.1	3.5	5	6.5	6.8	15	12.8	12.8	25	23.7	22.9
-4	3.3	3.8	6	7.0	7.3	16	13.6	13.6	26	25.1	24.2
-3	3.6	4.1	7	7.5	7.7	17	14.5	14.5	27	26.6	25.6
-2	3.9	4.4	8	8.0	8.1	18	15.5	15.4	28	28.3	27.0
-1	4.2	4.6	9	8.6	8.8	19	16.5	16.2	29	29.9	28.6
0	4.6	4.9	10	9.2	9.4	20	17.5	17.2	30	31.7	30.1

## XVII

## GLAISHER'S HYGROMETRIC FACTORS

READING OF DRY BULB	FACTOR	READING OF DRY BULB	FACTOR	READING OF DRY BULB	FACTOR	READING OF DRY BULB	FACTOR
$^{\circ}$ F.		$^{\circ}$ F.		$^{\circ}$ F.		$^{\circ}$ F.	
22	7.60	42	2.23	62	1.86	82	1.67
24	6.92	44	2.18	64	1.83	84	1.66
26	6.08	46	2.14	66	1.81	86	1.65
28	5.12	48	2.10	68	1.79	88	1.64
30	4.15	50	2.06	70	1.77	90	1.63
32	3.32	52	2.02	72	1.75	92	1.62
34	2.77	54	1.98	74	1.73	94	1.60
36	2.50	56	1.94	76	1.71	96	1.59
38	2.36	58	1.90	78	1.69	98	1.58
40	2.29	60	1.88	80	1.68	100	1.57

## XVIII

## WET AND DRY BULB HYGROMETER

AIR TEMP.	DIFFERENCE BETWEEN WET AND DRY BULBS IN °C.										
	0	1	2	3	4	5	6	7	8	9	10
°C.	SATURATION PRESSURES IN MM. OF MERCURY										
0	4.6	3.7	2.9	2.1	1.3						
2	5.3	4.4	3.6	2.7	1.9	1.1	0.3				
4	6.1	5.2	4.3	3.4	2.6	1.8	0.9				
6	7.0	6.0	5.1	4.2	3.3	2.4	1.6				
8	8.0	7.0	6.0	5.0	4.1	3.2	2.3	1.4	0.6		
10	9.2	8.1	7.0	6.0	5.0	4.0	3.1	2.2	1.3		
12	10.5	9.3	8.2	7.1	6.0	5.0	4.0	3.0	2.1	1.2	0.3
14	11.9	10.7	9.4	8.3	7.1	6.1	5.0	4.0	3.0	2.0	1.1
16	13.5	12.2	10.9	9.7	8.4	7.3	6.3	5.0	4.0	3.0	1.9
18	15.4	13.9	12.5	11.2	9.9	8.6	7.4	6.3	5.1	4.0	3.0
20	17.4	15.9	14.3	12.9	11.5	10.2	8.8	7.6	6.4	5.2	4.1
22	19.7	18.0	16.4	14.8	13.3	11.9	10.5	9.1	7.8	6.6	5.4
24	22.2	20.4	18.6	17.0	15.3	13.8	12.3	10.9	9.4	8.1	6.8

For intermediate temperatures take proportional values.

## XIX

## CRITICAL TEMPERATURES

Helium .. ..	— 268° C.	Carbon dioxide ..	31.1° C.
Hydrogen .. ..	— 234.5° C.	Ammonia .. ..	130° C.
Nitrogen .. ..	— 146° C.	Sulphur dioxide ..	155.4° C.
Air .. ..	— 140° C.	Water .. ..	365° C.
Oxygen .. ..	— 118° C.		

## XX

## THERMAL CONDUCTIVITIES

Values are at ordinary temperatures, in c.g.s. units.

Silver .. ..	0.974	Bismuth .. ..	0.0194
Copper .. ..	0.918	Ice .. ..	0.005
Gold .. ..	0.700	Glass (soft) .. ..	0.00155
Zinc .. ..	0.265	Water .. ..	0.00131
Brass .. ..	0.260	Oak .. ..	0.0006
Platinum .. ..	0.166	Cardboard .. ..	0.0005
Iron .. ..	0.161	India-rubber .. ..	0.00045
Tin .. ..	0.155	Ebonite .. ..	0.00042
Steel .. ..	0.115	Hydrogen .. ..	0.00041
Lead .. ..	0.083	Felt .. ..	0.00009
Mercury .. ..	0.0197	Air .. ..	0.000058

## XXI

REFLECTING POWERS OF SURFACES FOR RADIATION FROM  
A BODY AT 100° C.*Brass is taken as 100.*

Brass .. ..	100	Steel .. ..	70
Silver .. ..	90	Glass .. ..	10
Tin .. ..	80	Lampblack .. ..	0

XXII.—DIATHERMANCIES OF SOLIDS. (*See p. 342.*)

SUBSTANCE	OIL FLAME (ARGAND LAMP WITHOUT CHIMNEY)	INCANDESCENT PLATINUM, HEATED BY SPIRIT LAMP	BLACKENED COPPER, HEATED TO 390° C.	BLACKENED COPPER, HEATED TO 100° C.
Rock-salt (clear)	92	92	92	92
Iceland spar ..	39	28	6	0
Mirror glass ..	38	25	6	0
Quartz (clear) ..	37	28	6	0
Amber (artificial)	21	5	0	0
Borax .. ..	18	12	8	0
Alum (crystals) ..	9	2	0	0
Ice .. ..	6	0	0	0

XXIII.—DIATHERMANCIES OF LIQUIDS. (*See page 343.*)

	PERCENTAGE TRANSMITTED
Cell alone .. ..	Taken as 100
Cell containing:—	
Block of mirror glass, 1 cm. thick ..	53
Carbon bisulphide .. ..	63
Essence of turpentine .. ..	31
Pure sulphuric acid .. ..	17
Absolute alcohol .. ..	15
Alum water .. ..	12
Distilled water .. ..	11

## XXIV.—EMISSIVE POWERS AT 120° C.

Lampblack .. ..	100	Platinum (polished) .. ..	9.5
White lead .. ..	100	Copper foil .. ..	4.9
Paper .. ..	98	Gold leaf .. ..	4.3
Glass .. ..	90	Silver (chemically deposited) ..	5.4
India ink .. ..	85	Silver (ditto, polished) ..	2.2

## XXV.—RELATIVE ABSORBING POWERS AT 100° C.

Lampblack .. ..	100	India ink .. ..	85
White lead .. ..	100	Shellac .. ..	72
Isinglass .. ..	91	Metals .. ..	13

## ANSWERS TO EXERCISES

**EXERCISES II.** (*Page 373.*)

1.  $-40^{\circ}\text{F.}$
2.  $36^{\circ}\text{F.}, 68^{\circ}\text{F.}$
3.  $1562^{\circ}, 21.2^{\circ}, -58^{\circ}\text{F.}; 680^{\circ}, -4.8^{\circ}, -40^{\circ}\text{R.}$
4.  $1110^{\circ}, -2.8^{\circ}, -23.3^{\circ}, -45^{\circ}\text{C.}; 88^{\circ}, -2.2^{\circ}, -18.7^{\circ}, -36^{\circ}\text{R.}$
5.  $137.5^{\circ}, -10^{\circ}, -33.75^{\circ}\text{C.}; 279.5^{\circ}, 14^{\circ}, -28.75^{\circ}\text{F.}$
6.  $-0.04^{\circ}, -0.22^{\circ}, -0.5^{\circ}\text{C.}$

**EXERCISES III.** (*Page 373.*)

1.  $20.59^{\circ}\text{C}$ .
2.  $\frac{R_t}{R_0} = 1 + 0.003064t - 0.00000051t^2$ ;  $\delta = 1.65$ .

**EXERCISES IV.** (*Page 373.*)

1. 1.0057 cubic decimetre.      2. 0.065 in.      3. 0.000016.  
4. 0.03 cm.      5. 0.0000258; 0.0000086.  
6. 1.0015 pint.      7. 10.17 grm.      8. 2.036 : 1.

**EXERCISES V.** (*Page 374.*)

- [illegible]

**EXERCISES VI.** (*Page 375.*)

- |                |                |                  |
|----------------|----------------|------------------|
| 1. 2 litres.   | 2. 568 mm.     | 3. 476 c.c.      |
| 4. 860 c.c.    | 5. 0.0038.     | 6. 664° C.       |
| 7. 0.084 gram. | 8. 1.0043 : 1. | 9. 313° C.       |
| 10. — 459° F.  | 11. 534 c.c.   | 12. 451 cub. in. |

**EXERCISES VII.** (*Page 376.*)

- |              |                          |            |
|--------------|--------------------------|------------|
| 1. 11.1.     | 2. 14.2° C.              | 3. 52° C.  |
| 4. 0.057.    | 5. 0.214.                | 6. 0.64.   |
| 7. 4.79 grm. | 8. 756° C.               | 9. 0.0963. |
| 10. 0.615.   | 11. 1.005, 1.027, 1.016. |            |
| 12. 3.49.    | 13. 0.478.               | 14. 56.    |

## EXERCISES VIII. (Page 377.)

- |                    |                   |                           |
|--------------------|-------------------|---------------------------|
| 1. 171.4 calories. | 2. 67° C.         | 3. 78.8 calories per grm. |
| 4. 0.033.          | 5. 44.4 calories. | 6. 0.11.                  |
| 7. 0.917.          | 8. 0.033.         |                           |

## EXERCISES IX. (Page 378.)

- |                                       |                          |
|---------------------------------------|--------------------------|
| 1. 506 mm.; 673,000 dynes per sq. cm. | 2. 537 calories per grm. |
| 3. 65.3° C.                           | 4. 538 calories per grm. |
| 6. 2020 calories.                     | 7. 35.1° C.              |
|                                       | 8. 0.187.                |

## EXERCISES X. (Page 378.)

- |                |  |              |
|----------------|--|--------------|
| 1. 803 mm.     | 2. 742.4 mm.                                       | 3. 1117 c.c. |
| 4. 0.0242 c.c. | 5. Doubles; becomes infinitely large, i.e. bursts. |              |
| 6. 4 approx.   | 7. 9.1.  | 8. 118.5.    |
| 9. 58.2.       |  |              |

## EXERCISES XI. (Page 379.)

- |               |               |              |
|---------------|---------------|--------------|
| 1. 84%.       | 2. 52.9%.     | 3. 1.5° C.   |
| 4. 1.205 grm. | 5. 0.017 grm. | 6. 90.6 c.c. |

## EXERCISES XII. (Page 379.)

- During evaporation and the uplifting of clouds, heat energy becomes potential and kinetic energy. When the rain reaches the earth again, all the potential energy and nearly all the kinetic energy has disappeared.
- Chemical energy in coal  $\rightarrow$  Heat energy of flames and water  $\rightarrow$  Kinetic energy of train and passengers  $\rightarrow$  Kinetic energy of air and heat energy of rails and rubbing parts of wheels.
- 5 water lb. degree C.
- 1° C., 1.8° F.
- 1390 ft.-lb.
- 5.9%.
- 165 lb.
- 700 ft.-lb.;  $2.09 \times 10^7$  ergs.
- 112,000 ft.-lb. per lb.;  $335 \times 10^7$  ergs per grm.; 752,000 ft.-lb. per lb.;  $2250 \times 10^7$  ergs per grm.
- $2.87 \times 10^7$  ergs;  $2.93 \times 10^4$  grm. cm.
- $S_p = 0.237$ ;  $S_s = 0.168$ .
- 0.53 ohm.

## EXERCISES XIII. (Page 380.)

- |   |                                |
|---|--------------------------------|
| 1. 2005 mm.; 1520 mm.                                       | 2. 425° C.; 25.59 atmospheres. |
| 3. -57.2° C.  |                                |
| 4. 0.14 increase; Final pressure = 0.832 original pressure. |                                |
| 5. $4.18 \times 10^7$ ergs.                                 | 6. 3.429; 2.443.               |
| 7. 1.42.  |                                |

## EXERCISES XVI. (Page 381.)

- |                                |                  |            |
|--------------------------------|------------------|------------|
| 1. $5.2 \times 10^7$ calories. | 2. 1.525.        | 3. 0.0384. |
| 4. $1.8 \times 10^7$ calories. | 5. 125 calories. |            |
| 6. 0.00013 c.g.s. unit.        | 7. 0.067.        |            |



## EXERCISES XVII. (Page 381.)

1. 13%.      2. 2.56%.      3.  $10^{\frac{1}{24}}$ ; No.      4. 1000 grm.

## EXERCISES XVIII. (Page 382.)

1. 49,300 cm. per sec.      2. 46,600 cm. per sec.  
 2.  $200 \times 10^6$  ergs.      4.  $3.04 \times 10^1$  ergs.  
 5.  $\frac{1}{18}$ .      6.  $2.084 \times 10^{18}$  ergs per kilogram.

## EXAMINATION QUESTIONS. (Page 383.)

4.  $-0.4^\circ \text{C}$ .      9.  $2.22 \times 10^{10}$  grm. wt.  
 10.  $1.37 \times 10^{-5}$  per  $^\circ \text{C}$ .      11.  $86^\circ \text{C}$ .      12. 694.5 c.c.  
 13.  $329.7^\circ \text{C}$ .      17. 0.94 grm.  
 18.  $\frac{W_t - W_0}{(W - W_0)t}; \frac{W_t - W_0}{(W - W_0)t} + \frac{W - W_0}{W - W_t} \beta$ .  
 20. 77.8 cm.      22.  $2.62 \times 10^6$  ergs per grm.      23. 67.38 cm.  
 28.  $84.1^\circ \text{C}$ .      31. (a) 80.6 cal. per grm.; (b) 0.47.  
 33. 0.43.      34. 0.116 cal. per min.  
 38. 1617.7 grm.      40. 2.17.      42. 55.625 lb.  
 44. 907.13 c.c.      45. 554.9 mm.  
 46. Vapour pressure = 15 mm. of mercury.      47. 449 mm.  
 49. 1575 mm.      52. 10.274 grm.      53. 1210.2 grm.  
 55. 17.28 mm.      56. 1161.9 Kgm.      58.  $0.072^\circ \text{C}$ .  
 60. 59.07.      61. 70,994 cm. per sec.      64. 0.069.  
 65. 4.54 atmospheres.      66. 37.92 cm.      71. 79.7 cm. of mercury.  
 77.  $4.545^\circ \text{C}$ ;  $95.445^\circ \text{C}$ ; 68.2 calories.      78. 0.0134.  
 81. 0.5 c.g.s. units.      82.  $98.7^\circ \text{C}$ .      83. 0.00119 c.g.s. units.  
 84. 51.05 H.-P. per sec.      94. 5; 0.26.      95. 1.95 : 1.  
 98. 184,000 cm. per sec.      100.  $409^\circ \text{C}$ .      101. 501.9 cal.  
 102. (a)  $2.496 \times 10^{10}$  ergs; (b)  $1.248 \times 10^{10}$  ergs; (c)  $0.946 \times 10^{10}$  ergs.

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